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# THE ANALYST

A Monthly Publication  
dealing with all branches  
of Analytical Chemistry:  
the Journal of the Society  
for Analytical Chemistry

Editor: J. B. ATTRILL, M.A., F.R.I.C.

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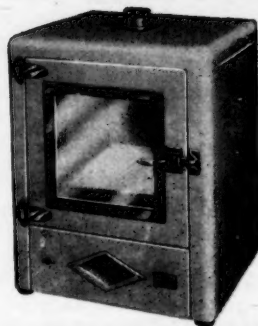
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# THE ANALYST

## PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

### ANNUAL GENERAL MEETING

THE eighty-fourth Annual General Meeting of the Society was held at 4.30 p.m. on Wednesday, February 26th, 1958, in the meeting room of the Royal Society, Burlington House, London, W.1. The Chair was occupied by the President, Dr. J. H. Hamence, M.Sc., F.R.I.C. The financial statement for the year ending October 31st, 1957, was presented by the Honorary Treasurer and approved, and the Auditors for 1958 were appointed. The Report of the Council for the year ending February, 1958 (see pp. 253-261), was presented by the Honorary Secretary and adopted.

The Scrutineers, Mrs. H. I. Fisk and Mr. H. E. Brookes, reported that the following had been elected officers for the coming year—

*President*—J. H. Hamence, M.Sc., Ph.D., F.R.I.C.

*Past Presidents serving on the Council*—D. W. Kent-Jones, J. R. Nicholls, George Taylor and K. A. Williams.

*Vice-Presidents*—N. L. Allport, R. C. Chirnside and A. A. Smales.

*Honorary Treasurer*—A. J. Amos.

*Honorary Secretary*—R. E. Stuckey.

*Honorary Assistant Secretary*—S. A. Price.

*Other Members of Council*—The Scrutineers further reported that 501 valid ballot papers had been received and that votes had been cast in the election of Ordinary Members of Council as follows—J. Haslam, 348; W. T. Elwell, 309; G. W. C. Milner, 308; T. S. West, 305; R. A. Chalmers, 281; E. I. Johnson, 247; P. J. C. Haywood, 224; H. A. Williams, 214; F. C. Hymas, 205; H. C. Smith, 199.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—R. A. Chalmers, W. T. Elwell, J. Haslam, E. I. Johnson, G. W. C. Milner and T. S. West.

W. Cule Davies, D. C. Garratt, H. M. N. H. Irving, E. Q. Laws and J. G. Sherratt, having been elected members of the Council in 1957, will, by the Society's Articles of Association, remain members of the Council for 1958.

A. N. Leather (Chairman of the North of England Section), Magnus A. Pyke (Chairman of the Scottish Section), S. Dixon (Chairman of the Western Section), R. Belcher (Chairman of the Midlands Section), D. F. Phillips (Chairman of the Microchemistry Group), R. A. C. Isbell (Chairman of the Physical Methods Group) and S. K. Kon (Chairman of the Biological Group) will be *ex-officio* members of the Council for 1958.

After the business outlined above had been completed, the meeting was opened to visitors, and Sir Hugh Linstead, O.B.E., LL.D., F.P.S., M.P., delivered the Bernard Dyer Memorial Lecture (see pp. 275-283). At the close of the meeting the President presented Sir Hugh with the Bernard Dyer Memorial Medal.

### JOINT MEETING

A JOINT Meeting of the Society and the Southern Region of the Association of Clinical Biochemists was held at 7 p.m. on Wednesday, May 7th, 1958, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President of the Society, Dr. J. H. Hamence, M.Sc., F.R.I.C., who was introduced by Mr. C. F. M. Rose, A.R.I.C., Chairman of the Southern Region of the Association of Clinical Biochemists.

The subject of the meeting was "Electrophoresis in Clinical Biochemistry" and the following papers were presented and discussed: "Basic Principles and Main Requirements

for Satisfactory Electrophoresis," by Professor Nicholas H. Martin, M.A., B.Sc., B.M., M.R.C.P., F.R.I.C.; "Paper Electrophoresis of Lipoproteins," by W. G. Dangerfield, Ph.D., M.R.C.S., L.R.C.P.; "The Clinical Application of Electrophoresis," by A. L. Latner, M.D., M.Sc., M.R.C.P., F.R.I.C.

### NEW MEMBERS

#### ORDINARY MEMBER

Michael George Ashley, F.R.I.C., F.P.S.

#### JUNIOR MEMBERS

Philip S. Chen, jun., B.A. (Clark), Ph.D. (Rochester); James Murphy; Alan George Sinclair, B.Sc. (Aber.).

### DEATH

WE record with regret the death of

William Macro Seaber.

### NORTH OF ENGLAND SECTION

A JOINT Meeting of the Section and the Tees-side Local Section of the Royal Institute of Chemistry was held at 8 p.m. on Friday, March 28th, 1958, at the William Newton School, Junction Road, Stockton-on-Tees. The Chair was taken by the Chairman of the North of England Section, Mr. A. N. Leather, B.Sc., F.R.I.C., at the invitation of Mr. H. N. Wilson, F.R.I.C., Chairman of the Tees-side Local Section.

The following paper was presented and discussed: "Residues in Foods Deriving from Processing Hygiene and Manufacturing Aids," by J. B. M. Coppock, B.Sc., Ph.D., F.R.I.C., and R. A. Knight, B.Sc., F.R.I.C.

### SCOTTISH SECTION

AN Ordinary Meeting of the Section was held at 6.50 p.m. on Monday, March 24th, 1958, in the Royal College of Science and Technology, 204 George Street, Glasgow, C.I. The Chair was taken by the Chairman of the Section, Dr. Magnus Pyke, F.R.I.C., F.R.S.E.

Following an introductory talk by him, a film on "Polarography" was shown by Dr. J. Masek of the Czechoslovak Polarographic Research Institute, Prague.

### WESTERN SECTION

THE Section participated in a meeting of the South-Western Counties Section of the Royal Institute of Chemistry held at 5.30 p.m. on Friday, February 21st, 1958, in the Technical College, Plymouth. The Chair was taken by the Vice-Chairman of the South-Western Counties Section, Mr. T. W. Parker, F.R.I.C.

A lecture on "New Techniques in Qualitative Analysis" was given by D. W. Wilson, M.Sc., F.R.I.C.

### MIDLANDS SECTION

AN Ordinary Meeting of the Section was held at 6.30 p.m. on Thursday, March 20th, 1958, in the Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F.

A discussion on "The Determination of Toxic Substances in the Atmosphere" was opened by J. C. Gage, B.Sc., Ph.D., F.R.I.C.

### MICROCHEMISTRY GROUP

THE fourteenth London Discussion Meeting of the Group was held at 6.30 p.m. on Wednesday, March 19th, 1958, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Honorary Secretary of the Group, Mr. D. W. Wilson, M.Sc., F.R.I.C.

A discussion on "The Microdetermination of Carbon, Hydrogen and Nitrogen in the Presence of Interfering Elements" was opened by G. Ingram, A.R.I.C.

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## BIOLOGICAL METHODS GROUP

A DEMONSTRATION Meeting of the Group was held at 6.30 p.m. on Wednesday, March 26th, 1958, in the Physiology Laboratory, University College, Gower Street, London, W.C.1. The Chair was taken by the Chairman of the Group, Dr. S. K. Kon, F.R.I.C.

The following pieces of apparatus were demonstrated—

Apparatus and techniques used in plate assays—Joy Stephens and Pat Whitmore.

(a) Semi-automatic plate punching machine; (b) large-plate levelling screws; (c) a nomogram for 2:1 and 4:1 dose-ratio plate assays (Miyamura)—J. S. Simpson.

Automatic press-button filling machine delivering 1 to 5 ml—P. L. Gibbon.

Device for speeding up turbidity readings using a Spekker absorptiometer—P. L. Gibbon.

Apparatus for photographing plates—D. Lawson.

Comparison of agar gel for assay media—W. H. Pierce.

Membrane filtration—W. H. Pierce.

The use of large plates in routine bacteriological methods—A. H. Sexton.

The assay of choline by disc plate—E. C. Barton-Wright.

The assay of diastase by large-plate methods—R. E. Duncombe.

The assay of synergistin components of the antibiotic E129 complex—Christine J. Bessell.

Estimation of the activity of drugs against *Leishmania donovani*—Kathleen R. Heath and Jean Fisher.

Microbiological assay of mercury compounds—R. E. Duncombe.

Microbiological assay of mixtures of streptomycin and dihydrostreptomycin—J. P. Jefferies and J. S. Simpson.

The standardisation of freeze-dried B.C.G. vaccine—Pauline Farmer, J. Dudley and P. W. Muggleton.

Vitamin B<sub>12</sub> antagonists—W. F. J. Cuthbertson and H. F. Pegler.

Automatically controlled isolated-organ bath—J. L. Mongar.

Automatic apparatus for controlling infusions during digitalis assays—L. Hall and K. L. Smith.

Antidiuretic assay—S. E. Dicker.

Assessment of anti-inflammatory drugs—G. F. Somers.

Simple methods for testing analgesic drugs—G. F. Somers.

Automatic scanner of labelled chromatograms—F. P. W. Winteringham.

## SUMMARIES OF PAPERS PRESENTED AT MEETINGS OF THE SOCIETY

THE following are summaries of the papers presented at the Ordinary Meeting of the Society organised by the Microchemistry Group on Friday, February 7th, 1958, in London. A first report appeared in *The Analyst*, 1958, 83, 65.

The papers were: "Applications of the Conway Diffusion Technique to the Analysis of Radioactive Materials for Trace Impurities," by J. K. Foreman, B.Sc., A.R.I.C.; "The Use of Long-chain Quaternary Amine Salts in the Solvent Extraction of Metal Ions," by R. Powell, A.R.I.C.

## APPLICATIONS OF THE CONWAY DIFFUSION TECHNIQUE TO THE ANALYSIS OF RADIOACTIVE MATERIALS FOR TRACE IMPURITIES

MR. J. K. FOREMAN described work carried out in the U.K.A.E.A. laboratories at Windscale utilising the Conway diffusion technique for determining trace amounts of certain non-metallic elements in plutonium. This technique, in which the trace element was liberated as a volatile compound, had a number of features that favoured its use for the analysis of radioactive materials. In particular, (i) the diffusion units were compact, and a number of analyses could be performed simultaneously in a small glove box, (ii) the diffusion unit was a closed system and the spread of radioactive contamination was effectively localised, (iii) little operator attention was required and (iv) the effect of variables associated with a particular analysis could be readily and quickly established by experiment, and could usually be supported by simple theoretical considerations of the dependence of the rate of absorption of the volatile compound upon the dimensions of the apparatus and the volume of solution from which it was liberated. The absorption time could be reduced to a minimum by forming the volatile compound in the minimum volume of solution and by using high concentrations of ionic components to "salt-out" the volatile compound.

Specific applications described were the determinations of chemically combined nitrogen, chlorine and sulphur in plutonium.

Nitrogen was liberated as ammonia from the outer compartment of the Conway unit by 6 N sodium hydroxide after dissolution of the metal in hydrochloric acid. The

ammonia was collected in hydrochloric acid in the inner compartment, and the determination was initially completed absorptiometrically by using the blue colour formed on the addition of sodium phenate, sodium hypochlorite and a trace of a manganous salt. This method was time-consuming, and in addition the sodium phenate was unstable; therefore an alternative finish, based on the titration of the excess of acid remaining after absorption of the ammonia, was substituted. Sulphuric acid, 0.01 *N*, incorporating the indicator (methyl red), was used as absorbent, and 0.01 *N* sodium hydroxide as the titrant.

The precipitate of plutonium hydroxide formed at the ammonia-liberation stage was shown not to occlude ammonia. The preparation of pure plutonium nitride (Brown, F., Ockenden, H. M., and Welch, G. A., *J. Chem. Soc.*, 1955, 4196) has permitted a rigid evaluation of the method.

For the determination of chlorine the plutonium was dissolved in 5 *N* sulphuric acid and the chlorine liberated by addition of a sulphuric acid - potassium permanganate oxidising mixture (which must be prepared in a bath of solid carbon dioxide to minimise its chlorine blank). After absorption in sodium hydroxide and conversion of hypochlorite to chloride, the latter was determined potentiometrically with silver nitrate, using a silver - silver amalgam electrode pair. This titration, at the microgram level, worked most satisfactorily in small volumes; 0.5 ml could be conveniently titrated in a platinum fluorimeter capsule, a change in potential of 40 to 50 mV occurring at the end-point.

For sulphur, a simple visual-comparison method was devised. The hydrogen sulphide liberated on dissolution of the metal in hydrochloric acid was absorbed in filter-paper impregnated with lead acetate solution. The brown stain formed was compared with stains produced by known amounts of sulphur.

#### THE USE OF LONG-CHAIN QUATERNARY AMMONIUM SALTS IN THE SOLVENT EXTRACTION OF METAL IONS

MR. R. POWELL said that, in recent years, use had been made of the long-chain amines and quaternary amines for the solvent extraction of certain anionic species, *e.g.*, the acid salts of many metals. Moore and his co-workers at ORNL had been particularly active in this field and had drawn attention to the similarity existing between this type of solvent extraction and separations with anion-exchange resins.

The principle involved was simple. The positively charged cations,  $\text{NR}_4^+$ , combined with the negatively charged anions, *e.g.*,  $\text{MnO}_4^-$  or  $\text{FeCl}_4^-$ , the resulting neutral compound being soluble in inert solvents such as benzene or chloroform. By suitable choice of acid medium many useful separations could be effected.

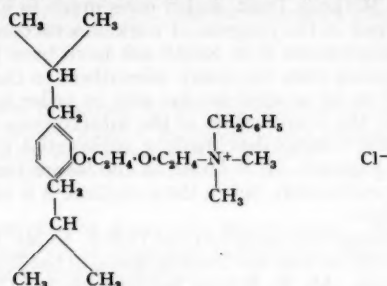
The principle had been applied to the separation and determination of plutonium in solutions of neutron-irradiated uranium. Normally such solutions contained a large excess of uranium and were highly radioactive. Operations had to be conducted behind shielding and the determination presented a difficult problem for the analyst. It was possible to determine the plutonium by counting the alpha particles emitted, but corrections had to be applied for other alpha emitters present, and it was necessary to know the isotopic composition of the plutonium before the count could be converted into a weight of metal. A more specific non-radiometric method was therefore sought.

Quadrivalent plutonium in nitric acid of concentrations greater than 7 *M* formed the acid complex  $\text{Pu}(\text{NO}_3)_6^{2-}$ . This could be retained on anion-exchange resins to separate it from uranium and most of the fission products, which do not form nitrate complexes in 7 *M* nitric acid. Recovery of the plutonium, however, was not quantitative. It could also be extracted into a number of solvents such as ethers, ketones and alkyl phosphates. Such extractions were not sufficiently selective for analytical application.

The long-chain quaternary ammonium salts were then examined for this purpose and were found to be extremely useful. The compounds were not available as pure reagents, but a variety was available in the form of industrial detergents. The nitrates of these compounds were insoluble in water, but were highly soluble in benzene or chloroform.

A 1 per cent. solution of the nitrate in benzene or chloroform was shaken with a nitric acid solution of quadrivalent plutonium. The plutonium was usually transferred quantitatively to the organic layer.

The most successful compound tested was Hyamine 1622, a Rohm and Haas product, stated to be *p*-diisobutylphenoxyethoxyethylmethylbenzylammonium chloride—



The partition coefficient for plutonium<sup>IV</sup> from 5 *M* nitric acid into benzene containing 1 per cent. of the nitrate was 200, the corresponding figure for uranium being 0.05. The beta-gamma activity of the extract showed a decrease of more than 10<sup>4</sup>, permitting the extract to be handled without heavy shielding.

Because of the very selective nature of the extraction it was possible to complete the determination by a less selective, though simple, colorimetric procedure. Thoronol [the sodium salt of 1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid] was a useful reagent for many quadrivalent metals. It was water soluble, but the acid could be extracted into benzene in the presence of a long-chain amine such as Hyamine 1622. The solution of plutonium in benzene was therefore combined with a solution of thoronol in the same solvent, in the presence of alcohol, and the resulting colour was measured on a Spekker absorptiometer. The limit of detection was about 1  $\mu$ g of plutonium.

## Annual Report of the Council: February, 1958

THE past year has been one of progress, and of consolidation for the many activities of the Society. It has also seen the completion of the first full year in the new headquarters. This concentration of the Society's activities at 14 Belgrave Square has been most beneficial, and the Council wishes to record its thanks to the Society of Chemical Industry for the help that it has given.

It is a pleasure to record the increasing activities of the Sections and Groups of the Society. The Conference of Honorary Secretaries has become an annual event and is of particular importance in arranging joint meetings between Groups and Sections. During the past year no fewer than six such joint meetings have been held, at Birmingham, Exeter, Cheltenham and Newport, as well as meetings in London. Two other meetings are worthy of comment, one held in March, 1957, jointly with the Fine Chemicals Group of the Society of Chemical Industry, the other in November, 1957, when Dr. Pfibil visited this country from Prague and addressed an audience of over 300 at the Royal Institution.

The report of the Scottish Section, given under a separate heading, contains a detailed account of the St. Andrews Congress held in June, 1957, but it is appropriate to refer to it here. There were nearly 300 registrations, including 30 from overseas, and many applications had to be refused owing to over-subscription. The Congress was particularly successful and its organisation was an outstanding achievement on the part of the Scottish Section. The Congress Proceedings will shortly be published. All concerned are to be congratulated.

The Midlands Section has also continued its many activities during the past year. It has, in addition, been extremely active, together with the Microchemistry Group, in its preparations for the Symposium on Microchemistry to be held in Birmingham in August, 1958. The patronage of the International Union of Pure and Applied Chemistry has been granted to this Symposium and the Council wishes it every success.

The activities of the Analytical Methods Committee are summarised separately, but it can be recorded that substantial progress has been made during the year. In particular the work of the Trade Effluents Joint Committee has been completed and it is intended that the

final booklet will be published in the Spring. The rapid progress achieved in this field is especially commendable. The Committee is fortunate in having Mr. Justice Lloyd-Jacob as Chairman of the Analytical Methods Trust, and it owes much to his direction of its financial affairs and to his lively interest in the progress of work. A successful three-year trial period has been completed—an achievement that would not have been possible without the very generous help during this period from the many subscribers to the Trust Fund. Its future work will, however, depend on an assured income and, in order to secure this, the Trustees are to appeal to Industry for the continuation of the subscriptions to the Trust Fund.

Once again the Chemical Council has made a substantial grant towards the cost of publication of the Society's journals. It is hoped in the future that the Society will be able to meet its own expenses of publication, but in the meantime it is with considerable gratitude that this grant is acknowledged.

Council records with pleasure the award of the O.B.E. to Mr. B. A. Ellis, Mr. A. Glover and Mr. R. S. Haskew. During the year the Meldola Medal of the Royal Institute of Chemistry was awarded to Dr. T. S. West. Dr. R. Belcher has been elected Chairman of the Analytical Section of the International Union of Pure and Applied Chemistry. Dr. K. A. Williams was appointed as one of the British Delegates to the Paris Conference of the International Union.

The Society now has 1900 members, an increase of 30 over the membership of a year ago. It is notable that this advance has occurred in spite of the recent increase in the annual subscription. The number of applications for membership continues to increase; during the year 1957, 122 new applicants were admitted to membership as compared with 117 and 108 for 1956 and 1955, respectively.

**LONG MEMBERSHIP**—The congratulations and good wishes of the Council are extended to S. Dixon and F. W. Edwards, who have completed 40 years of membership.

**DEATHS**—The Council regrets to have to record the deaths of the following members—

R. L. Barnard	L. H. Lampitt	F. Pugh
Lord Clinton (Honorary Member)	H. Lee	J. W. Skirvin
A. P. Davson	A. J. C. Lickorish	W. B. Walker
J. Gray	G. Roche Lynch	W. H. Woodcock
A. Harvey	A. E. Parkes	D. A. Yoxall
S. G. Kendrick		

**ORDINARY MEETINGS**—Six ordinary meetings of the Society were held during the year and the following papers were read and discussed—

**April, 1957, in London, organised by the Physical Methods Group, on Fluorimetry:**

"The Spectrometry of Fluorescence." By E. J. Bowen, M.A., D.Sc., F.R.S.

"Some Experiments with Spectrofluorimeters and Filter Fluorimeters." By C. A. Parker, B.Sc., Ph.D., F.R.I.C.

"Spectrofluorimetry." By Professor R. T. Williams, D.Sc., Ph.D.

"A Direct-reading Fluorimeter." By L. Brealey, B.Sc., and R. E. Ross, A.M.Brit.I.R.E.

**May, 1957, in London, organised by the Biological Methods Group, on the Estimation of Antibiotic Residues in Food:**

"Antibiotics and the Public Health." By J. M. Ross, M.B., Ch.B., D.P.H., D.Obst.R.C.O.G.

"The Determination of Antibiotics in Milk with Special Reference to Penicillin." By N. J. Berridge, B.Sc., Ph.D.

"The Determination of Antibiotic Residues in the Tissues and Body Fluids of Animals." By J. H. Taylor, Ph.D., M.R.C.V.S.

**October, 1957, in London:**

"The Analysis of 'Ferrites' by Means of EDTA." By D. G. Timms, B.Sc., A.R.I.C.

"The Determination of Mercury by Direct Distillation in its Compounds and Preparations." By H. E. Brookes, B.Sc., F.R.I.C., and L. E. Solomon, B.Sc.

"A System for the Determination of Certain Trace Metals in Crops." By W. D. Duffield.

"Some Applications of X-ray Spectrography." By H. I. Shalovsky, B.Sc., A.R.I.C.

**November, 1957, in London:**

"Recent Developments in Chelatometry." By Dr. Rudolf Přibil.

December, 1957, in London, discussion on Standardisation opened by:

R. C. Chirnside, F.R.I.C.

L. S. Theobald, M.Sc., A.R.C.S., F.R.I.C. (In Mr. Theobald's absence through illness, his contribution was read by Mr. Chirnside.)

J. Haslam, D.Sc., F.R.I.C.

G. Ingram, A.R.I.C.

February, 1958, in London, organised by the Microchemistry Group:

"Applications of the Conway Diffusion Technique to the Analysis of Radioactive Materials for Trace Impurities." By J. K. Foreman, B.Sc., A.R.I.C.

"The Use of Long-chain Quaternary Amine Salts in the Solvent Extraction of Metal Ions." By R. Powell, A.R.I.C.

**JOINT MEETING**—As mentioned above, the Society held a Joint Meeting with the Fine Chemicals Group of the Society of Chemical Industry in March, 1957, in London. The following paper was presented and discussed—

"Organic Reagents in Inorganic Analysis: Some Recent Developments." By H. M. N. H. Irving, M.A., D.Phil., D.Sc., F.R.I.C., L.R.A.M.

**NORTH OF ENGLAND SECTION**—The membership of the Section, at 391, shows no significant change. A questionnaire was circulated in the early part of the year to ascertain members' views with regard to future activities of the Section. This gave encouraging results and it is hoped that action being taken with these in mind will bear fruit in the coming year.

During the year, six meetings have been held, including the traditional Summer Meeting. Attendances at these were up to average. The following papers were read and discussed—

January, 1957, in Manchester:

"Recent Advances in the Analysis of Fertilisers." By H. N. Wilson, F.R.I.C.

March, 1957, in Liverpool:

"The Composition of Exhaust Gases." By A. Fitton, D.Sc., M.I.Chem.E.

May, 1957, in Llandudno:

"Some Chemical Features of the Composition of Fruit Juices." By V. L. S. Charley, B.Sc., Ph.D.

October, 1957, in Manchester:

Discussion Meeting on "The Analysis of Trade Effluents," opened by J. G. Sherratt, B.Sc., F.R.I.C.

November, 1957, in Widnes:

"Ion-exchange Chromatography Applied to Closely-related Organic Compounds" and "Trace-element Determinations with the Aid of Ion-exchange Membranes." By D. Logie, B.Sc.

December, 1957, in Liverpool:

"Present Trends in the Analysis of Feedingstuffs." By H. Pritchard, M.Sc., F.R.I.C.

**SCOTTISH SECTION**—The outstanding event of the past year was the St. Andrews Congress on Modern Analytical Chemistry in Industry held in June. Normal activities of the Section were not neglected, however, a full programme of meetings being arranged. In addition to the twenty-second Annual General Meeting held in Glasgow, at which various alterations to the Section Rules were passed for submission to Council for approval, four scientific meetings were held, two each in Glasgow and Edinburgh. As a member of the Federation of Chemical Societies in Glasgow, the Section was represented at the Ramsay Chemical Dinner. An innovation was the introduction of a discussion meeting into the programme, and for the first time a meeting has been held jointly with the Department of Chemistry of the University of Edinburgh, Dr. Pfibil's lecture and demonstration being ideal for this occasion.

The death of Mr. A. Dargie, one of the founder-members of the Scottish Section, is recorded with regret. The total membership of the Section is now 122.

The following papers have been presented and discussed—

Glasgow, February, 1957:

"Some Recent Developments in Analytical Chemistry." By R. Belcher, Ph.D., D.Sc., F.R.I.C., F.Inst.F.

**Edinburgh, March, 1957:**

- "Some Aspects of the Estimation of Uronic Acid in Carbohydrate Material." By D. M. W. Anderson, B.Sc., Ph.D., A.R.I.C.  
 "The Routine Semi-micro Determination of Molecular Weights." By J. Brooks, M.A., A.R.I.C., and A. F. Williams, B.Sc., F.R.I.C.

**St. Andrews, June, 1957:**

- "Analytical Chemistry in Industry." By J. Craik, M.A., B.Sc., Ph.D.  
 "Analytical Research in the Department of Scientific and Industrial Research in Relation to Industry." By G. R. Davies, B.Sc., M.Sc., Ph.D.  
 "Modern Analytical Methods in the Iron and Steel Industry." By B. Bagshawe, A.Met.  
 "Steelworks Analysis by Spectrographic Methods." By D. Manterfield, F.I.M.  
 "Chemical Problems in the Electrical Industry: The Contribution of Analysis as a Research Service." By R. C. Chirnside, F.R.I.C.  
 "The Application of Physical Methods of Analysis in the Gas Industry." By A. B. Densham, M.A., M.Inst.Gas E., and G. Gough, B.A.  
 "The Work of the Department of the Government Chemist." By G. M. Bennett, C.B., B.A., Ph.D., M.A., Sc.D., F.R.I.C., F.R.S.  
 "Analytical Developments in a Pharmaceutical Laboratory." By D. C. Garratt, D.Sc., Ph.D., F.R.I.C.  
 "Analysis and Food." By E. B. Hughes, D.Sc., F.R.I.C.  
 "Recent Progress in Separating Substances of High Molecular Weight." By R. L. M. Synge, B.A., Ph.D., F.R.S., Nobel Laureate.  
 "Emission Spectroscopy in Industrial Analysis." By M. Milbourn, B.Sc., A.R.C.S., F.Inst.P.  
 "Analysis in Medical Research." By A. T. James, B.Sc., Ph.D.  
 "The Analyst and Infra-red Spectroscopy." By A. E. Martin, D.Sc., Ph.D.  
 "Modern Analytical Chemistry in Relation to the Plastics Industry." By J. Haslam, D.Sc., F.R.I.C.  
 "Modern Analytical Chemistry and the Rarer Metals." By A. R. Powell, F.I.M., F.R.I.C., F.R.S.  
 "Analytical Research in the Nobel Division of Imperial Chemical Industries." By A. F. Williams, B.Sc., F.R.I.C.  
 "Process Analytical Control: The Problems of Manpower, Productivity and Automation." By B. W. Bradford, B.Sc., Ph.D., A.R.C.S., D.I.C., F.R.I.C., and D. L. Nicholson, B.A.  
 "New Analytical Reagents and their Applications in Industrial Plant-control Operations." By Professor G. F. Smith, Ph.D.  
 "The Use of Radioactive and Stable Isotopes in Industrial Analytical Problems." By A. A. Smales, B.Sc., F.R.I.C., and D. J. Ferrett, M.A., D.Phil.  
 "An Approach to Automatic Analytical Measurements." By D. A. Patient, B.Sc., A.Inst.P.  
 "Polarography." By G. C. Barker, M.A., Ph.D., G. W. C. Milner, M.Sc., A.Inst.P., F.R.I.C., and H. I. Shalvosky, B.Sc., A.R.I.C.  
 "The Application of Gas Chromatography in the Petroleum Industry." By Dr.-Ir. A. I. M. Keulemans.  
 "The Geochemical Approach to Prospecting for Minerals." By Professor C. F. Davidson, O.B.E., D.Sc., F.G.S., F.R.S.E.

**Glasgow, October, 1957:**

- Discussion Meeting on "The Estimation of Additives to Bread and Flour," opened by J. Sword, M.A., B.Sc., Ph.D., F.R.I.C., A. N. Harrow, A.H.-W.C., F.R.I.C., and H. C. Moir, B.Sc., F.R.I.C.

**Edinburgh, November, 1957, Joint Meeting:**

- "A New Line in the Development of Metal Indicators." By Dr. Rudolf Přibil.

**WESTERN SECTION**—The membership of the Section is 85.

The meetings have all been very well supported with an average attendance of about 40 members and lively discussions have followed the lectures. The Summer Meeting was very successful and was the first joint meeting held with another Section. The results were promising, and it has been decided to hold further meetings of a similar character. The policy of joint meetings with other chartered bodies has been maintained in outlying areas, the results proving very satisfactory. The following papers have been presented and discussed—

**Plymouth, January, 1957:**

- "Silicosis." By Professor E. J. King, M.A., Ph.D., D.Sc., F.R.I.C.

**Bristol, February, 1957:**

- "The Oxygen Demand of Trade Effluents with Respect to River Pollution." By C. J. Regan, B.Sc., F.R.I.C.

**Swansea, March, 1957:**

- "Some Recent Developments in Metallurgical Analysis." By G. W. C. Milner, M.Sc., A.Inst.P., F.R.I.C.

**Cheltenham, May, 1957, jointly with the Midlands Section:**

"Recent Advances in the Analysis of Plastics." By J. Haslam, D.Sc., F.R.I.C.

"The Analysis of Titanium, Zirconium and their Alloys." By W. T. Elwell, F.R.I.C.

"The Analysis of the Rarer Elements of Group III." By A. R. Powell, F.I.M., F.R.I.C., F.R.S.

**Exeter, September, 1957, jointly with the Microchemistry Group, on Some Applications of Microchemistry:**

"Applications to Paints and Pigments." By C. Whalley, B.Sc., F.R.I.C.

"Applications to Soils and Fertilisers." By B. M. Dougall, M.Sc., F.G.S., A.R.I.C.

Discussion on "The Use and Abuse of Microchemistry," opened by C. L. Wilson, D.Sc., Ph.D., F.R.I.C., and S. Bance, B.Sc., A.R.I.C.

**Newport, October, 1957, jointly with the Physical Methods Group:**

"Atomic Absorption Spectroscopy." By A. C. Menzies, M.A., D.Sc.

"Recording Flame Photometry." By L. Brealey, B.Sc.

**Bristol, November, 1957, jointly with the Association of Public Analysts:**

"Instrumentation in Radioactive Analysis." By E. Minshall, M.Sc., F.R.I.C.

"The Effects of Radiation on Living Cells." By H. F. Freundlich, M.A.

"Radioactivity in Sea Foods and Waters." By G. V. James, M.B.E., M.Sc., Ph.D., F.R.I.C., P.A.I.W.E.

"Radioactivity and its Detection in Effluents." By R. H. Burns, B.Sc., F.R.I.C.

**Salisbury, November, 1957:**

"Current Practice in Chemical Pathology." By I. MacIntyre, M.B., B.S.

**Newport, December, 1957:**

"Inorganic Chromatography." By F. H. Pollard, B.Sc., Ph.D.

**MIDLANDS SECTION**—The membership of the Section is 316, an increase of 9 during the year.

During 1957, 12 ordinary meetings have been held; of these, two were held jointly with the Birmingham and Midlands Section of the Royal Institute of Chemistry, one with the Microchemistry Group and one with the Physical Methods Group. A two-day meeting in Cheltenham was held jointly with the Western Section. The average attendance at meetings was 45. The following papers were presented and discussed—

**Birmingham, January, 1957:**

"The Analytical Chemistry of Some Newer Insecticides and Herbicides." By K. Gardner, B.Sc., F.R.I.C.

**Nottingham, January, 1957:**

"Some Contradictions and Discrepancies Concerning a Classical Method of Analysis." By R. Belcher, Ph.D., D.Sc., F.R.I.C., F.Inst.F.

**Birmingham, February, 1957, jointly with the Physical Methods Group, on High Frequency Titrations:**

"Instrumentation." By J. Allen, A.R.I.C.

"Applications." By E. S. Lane, B.Sc., Ph.D., F.R.I.C.

**Birmingham, March, 1957:**

"Thermo-gravimetric Analysis." By Professor C. Duval.

**Nottingham, March, 1957:**

"The Analysis of Complex Sulphur Compounds." By C. E. Kendall, B.Sc., A.R.I.C.

**Birmingham, April, 1957:**

"The Analytical Chemistry of Beryllium." By E. Booth.

**Birmingham, May, 1957, jointly with the Microchemistry Group, on The Microdetermination of Functional Groups:**

"Some Developments in the Analysis of Functional Groups." By W. I. Stephen, B.Sc., Ph.D., A.R.I.C.

"The Determination of N-Methyl Groups." By M. K. Bhatta, M.Sc., A.R.I.C.

"The Determination of Equivalents." By T. S. West, Ph.D., A.R.I.C.

"Titrations in Non-aqueous Media on the Sub-micro Scale." By T. S. West, Ph.D., A.R.I.C.

Cheltenham, May, 1957, jointly with the Western Section:

Details of the papers read at this meeting are given in the report on the Western Section.

Birmingham, September, 1957:

"The Determination of Some Inorganic Substances in Trade Effluents." By N. T. Wilkinson, F.R.I.C.

Birmingham, October, 1957:

"Analytical Methods in Clinical Biochemistry." By H. Varley, M.Sc., F.R.I.C.

Nottingham, October, 1957:

"The Analytical Chemistry of Morphine Poisoning." By A. S. Curry, M.A., Ph.D.

Birmingham, November, 1957:

"A New Line in the Development of Metal Indicators." By Dr. Rudolf Pribil.

Nottingham, December, 1957:

"Non-aqueous Titrations." By E. H. Tinley.

Birmingham, December, 1957:

"The Analytical Chemistry of Copper and its Alloys." By H. J. G. Challis, F.R.I.C., A.I.M.

**MICROCHEMISTRY GROUP**—The membership of the Group is now 618, an increase of 41 in the past year. During 1957 three ordinary meetings of the Group were held: in London (a meeting of the Society organised by the Group); in Birmingham (together with the Midlands Section) and in Exeter (together with the Western Section).

London, Micro-volumetric Analysis:

"Apparatus and Technique." By D. W. Wilson, M.Sc., F.R.I.C.

"Primary Standards." By R. Belcher, Ph.D., D.Sc., F.R.I.C., F.Inst.F. (Read by J. H. Thompson, B.Sc., Ph.D., A.R.I.C.)

"End-point Location." By E. Bishop, B.Sc., A.R.T.C., A.R.I.C.

Birmingham: The Microdetermination of Functional Groups:

The papers presented at this meeting are detailed in the report on the Midlands Section.

Exeter: Some Applications of Microchemistry:

The papers presented at this meeting are detailed in the report on the Western Section.

Six informal discussion meetings have been held, five in London and one in Exeter. The following topics were discussed—

Review of Previous Topics.

"The Microdetermination of Halogens," introduced by F. Oliver and R. Goulden, A.R.I.C.

"The Microdetermination of Functional Groups," introduced by W. I. Stephen, B.Sc., Ph.D., A.R.I.C., and G. Ingram, A.R.I.C.

"The Use and Abuse of Microchemistry," introduced by C. L. Wilson, D.Sc., Ph.D., F.R.I.C., and S. Bance, B.Sc., A.R.I.C. (At Exeter.)

"British Standards in Microchemistry," introduced by C. Meredith and G. Ingram, A.R.I.C.

"The Weighing and Measuring of Small Quantities," introduced by G. F. Hodsman, B.Sc., Ph.D., A.Inst.P., and R. Goulden, A.R.I.C. (Jointly with the Biological Methods Group.)

**PHYSICAL METHODS GROUP**—The membership of the Group is now 657, an increase of 30 since the last Annual Report.

During the past year the Group has held four Ordinary Meetings and also organised the April meeting of the Society. Two of the Group meetings were held in London and one each in Birmingham and Newport. The Birmingham meeting was held jointly with the Midlands Section and the Newport Meeting jointly with the Western Section. The meetings had an average attendance of over 45 members and visitors.

Following the Annual General Meeting on November 28th, 1956, W. Klyne, M.A., B.Sc., Ph.D., delivered a lecture entitled, "Optical Rotations in the Study of Organic Structures," and J. Evans described briefly and demonstrated a prototype model of a commercial photo-electric polarimeter. The following papers were read and discussed at other ordinary meetings of the Group—

High Frequency Titrations—Birmingham, February, 1957:

Details of the papers read at this meeting are given in the report on the Midlands Section.

**Electrochemistry—London, May, 1957:**

"Coulometric Titrations with an Integrated-current Source." By L. E. Smythe, M.Sc., Ph.D., A.R.I.C., F.R.A.C.I. (Read by G. W. C. Milner, M.Sc., A.Inst.P., F.R.I.C.)  
 "Pulse Polarography." By A. W. Gardner, B.Sc.

**Flame Photometry—Newport, October, 1957:**

Details of the papers read at this meeting are given in the report on the Western Section.

**BIOLOGICAL METHODS GROUP**—At present the membership of the Group is 293, an increase of 21 since last year. During the year the Committee has arranged two meetings for the presentation of papers, one of which was on behalf of the parent Society. In addition four Discussion Meetings have been held, together with a laboratory visit.

**November, 1956, London:**

Discussion on "Biological Assays in the Analytical Laboratory," introduced by K. L. Smith, M.P.S.

**January, 1957, London:**

Discussion on "The Relationship Between Statistics and Microbiological Assay," introduced by J. P. R. Toothill, B.Sc., A.R.I.C.

**March, 1957, London:**

Discussion on "The Experimental Assessment of Tranquillisers," introduced by A. Spinks, B.A., B.Sc., Ph.D., D.I.C.

**April, 1957, London:**

"Experience in the Microbiological Assay of Vitamins and Amino Acids by Large-plate Methods." By D. F. Harris and J. S. Simpson, F.I.M.L.T.  
 "Quantitative Analysis of Immunologically Specific Substances in Agar-gel Plates." By J. G. Feinberg, B.Sc., D.V.M., M.Sc.

**May, 1957, London, on Estimation of Antibiotic Residues in Food:**

Details of the papers read at this meeting are given in the report on the Ordinary Meetings of the Society.

**October, 1957, London:**

Discussion on "Biological Standards," introduced by J. W. Lightbown, M.Sc., Dip.Bact., F.P.S.

**ANALYTICAL METHODS COMMITTEE**—The work carried out by the Committee, Joint Committees and their Sub-Committees and Panels during the year shows that last year's progress has been maintained and there has been a steady output of recommended methods of analysis.

Two technical Reports were published by the Analytical Methods Committee, namely, the report of the Essential Oils Sub-Committee on the Determination of Linalol, in May, and the report of the Pesticides Residues in Foodstuffs Sub-Committee on the Determination of Total Organic Chlorine in Solvent Extracts of Vegetable Material, in June.

The A.B.C.M. - S.A.C. Joint Committee on Methods of Analysis of Trade Effluents has had a very active year and has now completed its programme of work. As was the practice last year, the methods were published in *The Analyst* as soon as they were approved, and these occupied a total of 64 pages as compared with 32 pages last year. All the methods have now been assembled and will be published as a complete booklet this Spring.

Difficulties were encountered in finding a method for silver in effluents that would be applicable for determining amounts of the order of 0.01 p.p.m. It was considered that the problem was worthy of further investigation and accordingly a grant by the Analytical Methods Trust has been made available to Dr. H. M. N. H. Irving to direct a short-term programme of research.

The four working Panels of the Joint Committee with the Pharmaceutical Society on Methods of Assay of Crude Drugs have continued with collaborative experimental work during the year, and a fifth Panel was appointed to investigate methods of assay of *Lonchocarpus* and *Derris*.

In the work of the Analytical Methods Committee itself, the Trace Elements in Fertilisers and Feeding-stuffs Sub-Committee has been reconstituted under the Chairmanship of Mr. C. J. Regan and is carrying out some collaborative trials of methods before final recommendations are made. Other Sub-Committees are continuing their investigations: the Metallic

Impurities in Organic Matter Sub-Committee and the Vitamin-E Panel are each preparing final reports.

Arrangements have been made with the Ministry of Agriculture, Fisheries and Food and the Association of British Insecticide Manufacturers to carry out collaborative experimental work on methods for determining residues of pesticides on foodstuffs; methods for BHC and DDT are to receive immediate attention.

A full Report of the Analytical Methods Committee covering the years 1955, 1956 and 1957 (*i.e.*, the first 3-year period since the Committee's reorganisation) is being prepared and will be published separately.

Mr. T. T. Gorsuch, the Society's first Research Scholar, has continued his work at Harwell under the able direction of Mr. A. A. Smales. The work has entailed the application of radiochemistry, using radioactive tracers as well as gamma spectrometry after neutron activation, (*a*) to the specific problem of defining the losses that can occur during the preparation of organic materials for trace-element analysis, investigating the causes of these losses and determining the optimum conditions for their elimination, and (*b*) to the various individual problems that have confronted the Metallic Impurities in Organic Matter Sub-Committee in its work.

**LIAISON COMMITTEE**—We record with pleasure that Dr. K. A. Williams was elected during the year to the General Council of the British Standards Institution.

During the year the following appointments were made—

**B.S.I. Committees:**

Mr. S. A. Price, Chemical Divisional Council.

Dr. S. G. Burgess, Methods of Test for Surface Active Agents.

Mr. P. J. C. Haywood, Standards for Pentachlorophenol, Determination of Tar Acids in Disinfectant Fluids.

Dr. H. Liebmann, Standardisation of Optical Cells and Colour Filters.

**Joint Library Committee, Chemical Society:**

Dr. J. G. A. Griffiths was again appointed the Society's representative.

**British Iron and Steel Research Association:**

Mr. R. C. Chirside and Dr. J. Haslam represented the Society at the Eleventh Chemists' Conference of the Methods of Analysis Committee (Metallurgy, General Division).

**Parliamentary and Scientific Committee:**

Mr. G. Taylor continued to represent the Society.

**Royal Institute of Chemistry, Summer School Organising Committee:**

Dr. J. Haslam and Mr. C. Whalley.

The Council of the Society thanks all its representatives for the work they have carried out in the various Committees and at varied meetings during the year.

**HONORARY TREASURER'S REPORT**—The accounts for the year ending October 31st, 1957, amply justify the decision of the Council to increase members' subscriptions and the prices of the Society's publications to outside subscribers. Despite the expense of moving into the new headquarters and of increasing the reserve for the decennial index, the deficit on each of the publication accounts before the receipt of the grant from the Chemical Council was reduced by over £1200. Furthermore, even in the absence of a grant from the Chemical Council, the over-all deficit would have been little over £1000 compared with a deficit of nearly £4000 in the absence of a grant in the previous year.

No doubt because we had thus attempted to put our house in order and because the sum we asked for was not great the Chemical Council met our request in full, and we are most grateful for this generous response to our appeal. Enabled thus to balance our publications account, we have in place of an over-all deficit a surplus of income over expenditure. This, however, is no reason for complacency. We cannot count on continued aid from the Chemical Council and indeed it is our desire to become self-supporting. We have made a move in this direction, but faced as we are already with increased costs for staff and for printing and

distribution and with requests for enlarged journals, we may be forced to increase again the cost of our publications to outside subscribers.

**THE ANALYST**—The 1957 volume contained 840 pages, compared with 732 in 1956. The numbers of papers and notes published in 1957 were 93 and 52, respectively, against 93 and 30 in 1956. One paper was a Review Paper.

When allowance is made for all matter other than papers and notes, and the Review Paper is excluded, the average length of a paper or a note is 4.7 pages. This is a fifth of a page greater than the average for 1956, which was itself the same as the 1954 figure. It seems necessary to repeat the warning given last year that it is essential to keep papers to the smallest possible size unless the publication of analytical knowledge is to suffer. A revised "Notice to Authors" intended to procure a reduction of the length of manuscripts has been issued during the year.

Besides the usual items, summaries of 8 papers presented at meetings but not being published in full in any journal were published in the Proceedings of the Society, one summary being in effect a short Review Paper. The Recommended Methods for the Analysis of Trade Effluents prepared by the Joint A.B.C.M. - S.A.C. Committee and published during the year occupied 64½ pages.

Ten issues of the Bulletin were distributed with *The Analyst* during the year, one of them being a special issue containing the programme of the Congress on Modern Analytical Chemistry in Industry at St. Andrews, organised by the Scottish Section.

Mr. N. C. Francis resigned the post of Assistant Editor at the end of October, 1957, and Mr. P. W. Shallis was appointed in his place. Mr. B. Harris has joined the editorial staff to fill the vacancy.

The number printed of each issue, 6400, appears to be adequate to meet demands and to leave a small stock of single parts available for purchase as back numbers, and for the first time in many years this number has not been increased. The total increase in the previous two years was 1100.

**ANALYTICAL ABSTRACTS**—*Analytical Abstracts* again showed an increase in size in 1957 as is shown by the following figures—

Year	Pages	Abstracts
1954	392	3190
1955	468	3556
1956	542	3820
1957	568	4223

The number of abstracts has increased in a greater proportion than the number of pages owing to the policy of reducing the length of the less important abstracts. The rate of payment to abstractors has been increased.

Mr. C. H. R. Gentry joined the Abstracts Committee in June, 1957.

The number of copies printed per month was 7000 from January to September inclusive. This was reduced to 6600 from October to December inclusive, but has again been raised to 7100 for January, 1958.

**CHEMICAL COUNCIL**—The increase in the price of *The Analyst* to outside subscribers greatly reduced the deficit in the Society's accounts. It was necessary, however, for the Society to apply to the Chemical Council for £1700 and £1050 in order to balance the accounts, respectively, of *The Analyst* and *Analytical Abstracts*. These amounts were paid in full, and the thanks of the Society are tendered to the Chemical Council for this grant.

**CONFERENCE OF HONORARY SECRETARIES**—Another successful meeting of the Honorary Secretaries of the Sections and Groups of the Society was held on May 22nd, 1957. These meetings are of value to all concerned and enable the President and Honorary Officers to discuss freely with the Honorary Secretaries all matters related to the organisation and future of the Society.

J. HAMENCE, *President*.

R. E. STUCKEY, *Honorary Secretary*.

## Report of the Analytical Methods Committee 1957

EACH of the two preceding annual Reports of the Analytical Methods Committee of the Society for Analytical Chemistry covered the work of one year. This present Report, however, reviews the three years that have elapsed since the Committee was reorganised as a self-supporting unit of the Society. This over-all account of the Committee's work is given because many of the subscribers to the Trust Fund, who so generously responded to the Society's appeal at the end of 1954, initially promised donations for three years to establish the Committee's work.

### GENERAL REVIEW

In the early part of 1957 the Committee was very sorry to lose, through resignation, Dr. J. R. Nicholls and Mr. N. L. Allport, both of whom had been valued members for many years, and the opportunity is taken here to thank them for all their help.

The Committee was glad to welcome in June Mr. E. Q. Laws and Mr. C. Whalley as their successors.

### PROGRESS OF WORK—

Originally the secretarial work of the Committee itself and each of its sub-committees and panels was undertaken voluntarily by one of the members, all of whom had full-time duties in their own spheres of work. Not only had it become necessary to relieve members of the onus of this secretarial work, but it became increasingly difficult to extend the field of investigation and a central paid secretariat became essential. This led to the Appeal to Industry to put the Committee on a sound financial basis. The present arrangement of having a small technical secretariat office within the Society's offices has been much appreciated by committee members and has facilitated co-ordination and enabled quicker progress to be made. Further, because the office also acts in an editorial capacity, the time between the completion of the collaborative work of a committee and the publication of its reports has been greatly reduced.

These advantages have been well demonstrated by the rapid progress of work by the Joint Committee on Methods for the Analysis of Trade Effluents set up by the Society and the Association of British Chemical Manufacturers in 1954. In view of Industry's need for recommended methods, the priority given to this work has maintained a steady output and ensured that the methods appeared in print as soon as possible after they were approved. The effort has been well rewarded, since the Joint Committee with its four working panels completed its entire programme (much of it entailing collaborative experimental work) by the end of 1957 and has published in *The Analyst* no less than 46 methods since the beginning of 1956. These, together with the remaining 6 methods just completed, are being collected and will be published in the Spring of 1958 as a complete volume of some 150 pages.

The Analytical Methods Committee itself has published 3 reports of original collaborative work carried out by its sub-committees—one of these, "The Estimation of Vitamin B<sub>12</sub>," was published in *The Analyst* in 1956 and the other two, "The Determination of Linalol in Essential Oils" and "The Determination of Small Amounts of Total Organic Chlorine in Solvent Extracts of Vegetable Material," in 1957. In other sub-committees, collaborative experimental work is still in progress, but it is expected that the results of some of this will be ready for publication in 1958.

The arrangement for investigating analytical problems by collaboration between two or more organisations, as exemplified by the work on the analysis of trade effluents, proved to be so satisfactory that another Joint Committee, this time with the Pharmaceutical Society, was set up in March, 1956, to prepare standard methods of assay of crude drugs and kindred materials, such as those that are used widely in commerce, but for which there are no standard or official methods at present in force. This Joint Committee immediately appointed four working panels to investigate chemical methods for digitalis, capsicum (capsaicin content), anthraquinone drugs and rauwolfia, respectively. A fifth panel, to investigate methods for the assay of lonchocarpus and derris, was appointed in July, 1957. All five panels are actively engaged in experimental work and it is interesting to note that each

panel has, from the first, turned its attention to a thorough study of the active ingredients of the crude drugs.

Further evidence of the value of joint investigations by several organisations has been the recent agreement by the Society (represented by the Analytical Methods Committee) to collaborate with the Association of British Insecticide Manufacturers and with the Scientific Sub-Committee on Poisonous Substances used in Agriculture and Food Storage of the Ministry of Agriculture, Fisheries and Food to test methods of analysis for pesticides residues in foodstuffs. In this investigation, the secretarial work is to be undertaken by the Ministry and *ad hoc* working panels are to be appointed when methods are considered ready for collaborative trial.

More detailed accounts of the work of the various Joint Committees, sub-committees and panels are given later in this Report.

#### ANALYTICAL METHODS TRUST—

The Committee is fortunate in having Mr. Justice Lloyd-Jacob as Chairman of the Analytical Methods Trust; it owes much to his direction of its financial affairs and to his lively interest in the progress of work.

A successful 3-year trial period has been completed—an achievement that would not have been possible without the very generous help during this period from the many subscribers to the Trust Fund. Its future work will, however, depend on an assured income; in order to secure this, the Trustees are to appeal to Industry for the continuation of the subscriptions to the Trust Fund.

#### RESEARCH GRANTS—

In the past, the work of a committee frequently suffered because members found it impossible to investigate problems fully, since the amount of work involved would have required concentrated research.

It was hoped, therefore, that the Trust Fund formed by subscriptions received as a result of the Appeal to Industry in 1954 would be large enough to allow some money to be set aside for research purposes after the secretariat's expenses had been met. It was most gratifying that the response was such that the first grant could be made a few months after the Committee was established on its new basis, with the result that a Research Scholar was appointed to carry out full-time work for a period of 2 years on a problem frequently encountered by analysts—namely, the causes of losses or accretions of some metals during the destruction of organic matter.

Again, at the end of 1957, it was possible to make a second grant to permit full-time research on the investigation of a problem that had arisen in the course of the work of the Joint Committee engaged in devising methods of analysis of trade effluents.

In addition to making these specific grants for research, it has been possible to help in the work of the Joint Committee that is investigating methods of assay of crude drugs by the purchase of special materials.

As the work of the various committees continues to expand, it is envisaged that further grants for research will be made in the near future.

*Research scholarship*—Mr. T. T. Gorsuch, the Society's first Research Scholar, was appointed at the beginning of 1956 to work at the Atomic Energy Research Establishment, Harwell, under the direction of Mr. A. A. Smales, and the Society is grateful to the Director of that Establishment for the facilities afforded there. The research is nearing completion and an account will shortly be published; it is also expected that the results will be of sufficient general interest to be the subject of a paper for presentation at one of the Society's meetings.

The research work has entailed the application of radiochemistry, by means of radioactive tracers as well as gamma spectrometry after neutron activation, (a) to the specific problem of defining the losses that can occur during the preparation of organic materials for trace-element analysis, investigating the causes of these losses and determining the optimum conditions for their elimination, and (b) to the various individual problems that have confronted the Metallic Impurities in Organic Matter Sub-Committee in its work.

*Research on methods for the determination of traces of silver*—The grant made recently by the Trustees is being used for research, under the direction of Dr. H. M. N. H. Irving

at Oxford, to devise a method for the determination of traces of silver in the presence of organic matter. This arose from the work of the Joint Committee on Methods for the Analysis of Trade Effluents, which indicated that, in the event of accidental contamination of rivers by silver, a method should be available for determining amounts down to 0.01 parts per million. It was envisaged that the work would take about 6 months.

#### INCOME AND EXPENDITURE—

The audited statement of accounts (see Appendix I) for the financial year ending October 31st, 1957, shows an expenditure of £4774. This figure includes expenses in connection with the Research Scholarship (the grant of £600 for research on silver analysis was not approved until after the end of the financial year) and shows an increase of £1419 over last year's figure.

The income from donations for 1957 amounted to £5900 received from 49 subscribers—about £450 less than was received in 1956.

Of the organisations that supported the original appeal in 1954, 17 per cent. entered into 7-year Deeds of Covenant and 33 per cent. promised annual donations for a period of 3 years; the remaining 50 per cent. of the subscribers preferred to consider the matter from year to year.

In view of the uncertain income derived in this way, the Trustees considered that it would be prudent to build up a reserve during the 3 years whilst the Committee established itself so that the various sub-committees and panels could be assured of the continuance of their work. For this reason, although the Committee's work has expanded steadily, a reasonable economy has been observed during this time and the secretariat staff of three has not been increased.

However, after the initial period in which considerable work has been undertaken, as can be seen from the report that follows, the potential value of the Committee's work to Industry has become apparent and an ever-increasing programme of work must be expected. This can only be done with an assured income. It is hoped that the support given by Industry will continue so that this more ambitious programme can be undertaken with confidence.

### REPORTS OF SUB-COMMITTEES OF THE ANALYTICAL METHODS COMMITTEE

#### ESSENTIAL OILS SUB-COMMITTEE

##### CONSTITUTION—

G. W. Ferguson, B.Sc., Ph.D., F.R.I.C.  
(Chairman)  
A. J. M. Bailey, B.Sc., F.P.S., F.R.I.C.  
D. Holness, B.A.  
H. T. Islip, B.Sc., F.R.I.C.  
P. McGregor, B.Sc., A.H.-W.C., F.R.I.C.  
J. H. Seager, M.Sc., F.R.I.C.  
G. E. Smith, B.Sc., F.R.I.C.  
B. D. Sully, B.Sc., Ph.D., A.R.C.S., F.R.I.C.

Analytical and Consulting Chemist  
W. J. Bush & Co. Ltd.  
Unilever Ltd., Central Perfumery Department  
Tropical Products Institute  
Department of the Government Chemist  
Yardley & Co. Ltd.  
Stafford Allen & Sons Ltd.  
A. Boake, Roberts & Co. Ltd.

##### PROGRESS OF WORK—

When the Analytical Methods Committee was reorganised in 1955, some sub-committees were automatically dissolved and subsequently reconstituted because the scope of work had been broadened. The original Essential Oils Sub-Committee, however, continued in being until the report of their collaborative work on methods for the determination of linalol had been completed. This report was eventually published in *The Analyst* in May, 1957.

The Sub-Committee was reorganised in February, 1957, under the Chairmanship of Dr. G. W. Ferguson. One meeting has since been held, and it was considered that the future programme of work would develop somewhat on requests for collaboration from the corresponding technical committee of the British Standards Institution.

#### MEAT PRODUCTS SUB-COMMITTEE

##### CONSTITUTION—

S. M. Herschdoerfer, Ph.D., F.R.I.C.  
(Chairman)  
S. Back, B.Sc., F.R.I.C.

T. Wall & Sons Ltd.  
Crosse & Blackwell Ltd.

Miss E. M. Chatt, B.Sc., F.R.I.C.

*British Food Manufacturing Industries Research Association*

C. D. Essex, A.M.Inst.B.E., F.R.I.C.

*Oxo Ltd.*

J. R. Fraser, B.Sc., A.C.G.F.C., F.R.I.C.

*Department of the Government Chemist*

H. G. Rees, B.Sc., Ph.D., A.R.C.S., D.I.C., F.R.I.C.

*Oxo Ltd.*

H. Amphlett Williams, Ph.D., A.C.G.F.C., F.R.I.C.

*Public Analyst*

TERMS OF REFERENCE—" (a) The determination of the meat content of products containing meat; (b) the determination of the constituents of meat and meat products.

NOTE—The term 'meat products' to include hydrolysed protein and, if found necessary, fish pastes."

#### PROGRESS OF WORK—

The previous Sub-Committee, under the name of the Meat Extracts Sub-Committee, was dissolved in 1955 and reconstituted with extended terms of reference and a title indicative of its wider scope.

Collaborative experimental work is being undertaken with particular reference to reviewing the values of the factors for nitrogen for various types of meat, since some dissatisfaction of existing values has frequently been expressed. The need for establishing values within closer limits than hitherto is directly associated with new legislation under the Food and Drugs Act, in which the meat content of sausages and meat pies might be stipulated; in this event reliable tests for compliance with the Act would be necessary.

In addition, methods for the determination of starch are under review during the collaborative tests.

#### METALLIC IMPURITIES IN ORGANIC MATTER SUB-COMMITTEE

##### CONSTITUTION—

T. McLachlan, D.C.M., A.C.G.F.C., M.I.Biol., F.R.I.C. (*Chairman*)*Public Analyst*

L. Brealey, B.Sc.

*Boots Pure Drug Co. Ltd.*

J. C. Gage, B.Sc., Ph.D., F.R.I.C.†

*Imperial Chemical Industries Ltd. (Industrial Hygiene Laboratories)*

C. L. Hinton, F.R.I.C.

*British Food Manufacturing Industries Research Association*

E. I. Johnson, M.Sc., F.R.I.C.

*Department of the Government Chemist*

W. C. Johnson, M.B.E., F.R.I.C.

*Hopkin & Williams Ltd.*

I. MacIntyre, M.B., Ch.B.

*University of London (Post-Graduate Medical School)*

R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.

*Analytical and Consulting Biochemist*

G. Taylor, O.B.E., F.R.I.C.\*

*Public Analyst, Official Agricultural Analyst and Consulting Chemist*

G. E. Willis, B.Sc., Ph.D., A.R.I.C.

*Imperial Chemical Industries Ltd. (Dyestuffs Division)*

\* Resigned—November, 1957.

† Elected—December, 1957.

TERMS OF REFERENCE—"To investigate the determination of small quantities of metals in organic matter."

#### PROGRESS OF WORK—

In the course of its work on the methods for both arsenic and lead, the Sub-Committee came to the conclusion that one of the chief reasons for variation in experimental results could be attributed to the losses or retention occurring during the destruction of organic matter. Accordingly it was decided that the reports on the trace metals should be confined to the method of determination of the element with only general reference to the preliminary treatment. Methods for the destruction of organic matter in general, with recommendations for appropriate procedure in particular cases, should be dealt with in a separate report, which is now under consideration.

The Sub-Committee came to the conclusion that the use of perchloric acid in the preliminary treatment of the sample should be encouraged and it has prepared a note for publication as a guide to the precautions that should be taken and the conditions under which perchloric acid may be used with safety.

Investigations into the molybdenum-blue method for the determination of arsenic are now in the final stage; after preliminary collaborative tests with simple solutions of arsenic, a series of tests on samples containing organic matter has been carried out and the results compared with those obtained by radiochemical methods at Harwell. A report on the work and on the method is in preparation.

Experimental work on the revised method for lead has been completed and it is hoped that the final report will be approved shortly.

The recommended methods for the determination of arsenic, lead and copper that were originally published as Analytical Methods Committee Reports have been reviewed by the Sub-Committee; that for arsenic (Gutzeit method) has been revised and approved for publication; those for copper and lead were considered to be out of date.

The Sub-Committee has been greatly assisted by the fundamental research done by Mr. Gorsuch at Harwell under the direction of Mr. Smales and is grateful to them also for their ready co-operation in helping to solve *ad hoc* problems in the course of the Sub-Committee's work.

#### DIRECT MICRO-DETERMINATION OF OXYGEN IN ORGANIC MATTER SUB-COMMITTEE

##### CONSTITUTION—

D. W. Wilson, M.Sc., F.R.I.C.

(Chairman)

G. C. Ackroyd, B.Sc., A.R.I.C.

P. R. W. Baker, B.Sc., A.R.I.C.

Miss B. B. Bauminger, Ph.D., A.I.R.I., F.R.I.C.

W. T. Chambers, B.Sc., Ph.D., A.R.I.C.

A. F. Colson, B.Sc., Ph.D., F.R.I.C.

Miss M. Corner, B.Sc., F.R.I.C.

R. R. Gordon, Ph.D.

G. Ingram, A.R.I.C.

F. J. McMurray

F. H. Oliver

H. J. Warlow

C. Whalley, B.Sc., F.R.I.C.

*Sir John Cass College (Department of Chemistry)*

*D.S.I.R., Fuel Research Station*

*Wellcome Research Laboratories*

*Dunlop Research Centre*

*British Rubber Producers' Research Association*

*Imperial Chemical Industries Ltd. (Alkali Division)*

*D.S.I.R., Chemical Research Laboratory*

*National Coal Board, Central Research Establishment*

*Courtaulds Ltd.*

*Wellcome Chemical Works*

*Parke, Davis & Co. Ltd.*

*D.S.I.R., Fuel Research Station*

*Laporte Chemicals Ltd.*

TERMS OF REFERENCE—"To investigate the Unterzaucher method, and its modifications for the micro-determination of oxygen."

##### PROGRESS OF WORK—

The Sub-Committee is nearing the end of its second series of collaborative tests in which, as a result of the preliminary investigation of differences of technique during the first series, the experiments have been designed with the object of reducing the "blank" values and of isolating possible sources of error. Because of the multiplicity of small modifications in technique that have been adopted from time to time by various laboratories, this second series of tests is very lengthy, but it is hoped that it will be possible to formulate a more closely defined technique as a result.

#### TRACE ELEMENTS IN FERTILISERS AND FEEDING-STUFFS SUB-COMMITTEE

##### CONSTITUTION—

C. J. Regan, B.Sc., F.R.I.C.

(Chairman)

S. M. Boden, B.Sc., A.R.I.C.

L. Brealey, B.Sc.

S. G. Burgess, B.Sc., Ph.D., F.Inst.Pet.,

M.Inst.S.P., F.R.I.C.

J. H. Hamence, M.Sc., Ph.D., F.R.I.C.

R. F. Milton, B.Sc., Ph.D., M.I.Biol., F.R.I.C.

R. L. Mitchell, B.Sc., Ph.D., F.R.S.E., F.R.I.C.

J. B. E. Patterson, M.Sc., F.R.I.C.

*Formerly Chemist-in-Chief, London County Council*

*Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service*

*Boots Pure Drug Co. Ltd.*

*London County Council*

*Public Analyst, Official Agricultural Analyst and Consulting Chemist*

*Analytical and Consulting Biochemist*

*Macaulay Institute for Soil Research (Department of Spectrochemistry)*

*Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service*

TERMS OF REFERENCE—"To devise appropriate methods of analysis (to be recommended for inclusion in the Regulations under the Fertilisers and Feeding Stuffs Act, 1926) for the determination of boron, cobalt, copper, fluorine, iodine, iron, magnesium, manganese, molybdenum, selenium and zinc, which can be expected to be present in fertilisers and feeding stuffs."

#### PROGRESS OF WORK—

The original Sub-Committee was not dissolved immediately after the reorganisation of the Analytical Methods Committee because it was hoped that it would be possible to proceed with the programme of work, although members were finding it increasingly difficult to devote sufficient time to the amount of research that was involved.

It was apparent that some of the methods that were being investigated by the Joint Committee on Methods for the Analysis of Trade Effluents might be applicable for fertilisers and feeding stuffs and it was decided to wait until these were published. Accordingly, after the appearance of these methods, during the past few months, the position was reviewed by the Analytical Methods Committee with the result that in September, 1957, the Sub-Committee was reconstituted under the Chairmanship of Mr. C. J. Regan. Since then 3 meetings have been held and considerable progress has already been made; collaborative experimental work is being carried out to check the suitability of selected published methods (including a number of those recommended for trade effluents) and to make any modifications that may be necessary.

#### VITAMINS

The original Vitamins Sub-Committee was dissolved at the time when the Analytical Methods Committee was reorganised, but the Panel on Vitamin E continues its investigations.

##### *Vitamin-E Panel*

#### CONSTITUTION—

A. L. Bacharach, M.A., F.R.I.C.

(Chairman)

J. Green, B.Sc., Ph.D., F.R.I.C.

(Honorary Technical Secretary)

V. H. Booth, Ph.D.

F. Brown, M.Sc., Ph.D.

A. R. Moss, B.Sc., Ph.D.

H. N. Ridyard, B.Sc., A.K.C., F.R.I.C.

P. W. Russell Eggitt, B.Sc., Ph.D., A.R.I.C.

C. A. Shacklady, B.Sc., A.R.I.C.

P. Stross, B.Sc.

G. Walley, B.Sc., F.R.I.C.

R. J. Ward, B.Sc., A.R.I.C.

E. C. Wood, B.Sc., Ph.D., A.R.C.S., F.R.I.C.

P. Harris, Ph.D.\*

*Consulting Chemist*

*Vitamins Ltd.*

*Medical Research Council, Dunn Nutritional Laboratory*

*Foot-and-Mouth Disease Research Institute*

*Roche Products Ltd.*

*Research Association of British Flour Millers*

*Spillers Ltd.*

*J. Bibby & Sons Ltd.*

*British Drug Houses Ltd.*

*Unilever Ltd.*

*Medical Research Council, Dunn Nutritional Laboratory*

*Public Analyst and Consulting Chemist*

*Distillation Products Industries, Rochester, New York, U.S.A.*

\* Corresponding member.

TERMS OF REFERENCE (OF ADVISORY PANEL)—"To survey the methods already proposed for the estimation of Vitamin E and to recommend to the [Vitamins] Sub-Committee a standard method or methods."

#### PROGRESS OF WORK—

During the year the Panel has been engaged in working out the manipulative details of a procedure for the differential micro-analysis of tocopherols in natural oils and in complex samples, such as poultry meals.

The method involves a paper-chromatographic separation of the tocopherols, after purification, followed by their individual assay by a modification of the Emmerie-Engel colorimetric method. Although a considerable amount of manipulative skill is required, the Panel is of the opinion that the method has many advantages; it is hoped that the final recommendations will be published soon as a Report.

# REPORT OF THE A.B.C.M. - S.A.C. JOINT COMMITTEE ON METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

## MAIN COMMITTEE

### CONSTITUTION—

#### *Representing the Association of British Chemical Manufacturers—*

H. N. Wilson, F.R.I.C.\*

(Chairman)

J. G. Maltby, B.Sc., F.R.I.C.\*

(Secretary)

F. G. Broughall, B.Sc., F.R.I.C.

D. C. Garratt, Ph.D., D.Sc., F.R.I.C.

I. S. Wilson, M.Sc., Ph.D., A.R.I.C.

#### *Representing the Society for Analytical Chemistry—*

J. H. Hamence, M.Sc., Ph.D., F.R.I.C.\*

L. Klein, M.Sc., Ph.D., M.Inst.S.P., F.R.I.C.

C. J. Regan, B.Sc., F.R.I.C.

J. G. Sherratt, B.Sc., F.R.I.C.

N. T. Wilkinson, F.R.I.C.

F.R.I.C.

Imperial Chemical Industries Ltd. (Billingham Division)  
Distillers Co. Ltd.

Midland Tar Distillers Ltd.  
Boots Pure Drug Co. Ltd.  
Monsanto Chemicals Ltd.

Public Analyst, Official Agricultural Analyst and Consulting Chemist  
Mersey River Board  
Formerly Chemist-in-Chief, London County Council  
Public Analyst and Consulting Chemist

Imperial Chemical Industries Ltd. (Alkali Division)  
Analytical and Consulting Chemist

J. S. Evans

Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.\*

Federation of British Industries

Secretary to the Analytical Methods Committee

\* Members of the Publications Sub-Committee, to which J. B. Attrill, M.A., F.R.I.C., Editor of *The Analyst*, has been co-opted.

TERMS OF REFERENCE—"To devise and recommend methods of analysis as applied to trade effluents, specifying in each case their applicability and limitations, but not the interpretation of the results of such tests as would be used to decide on the quality of an effluent."

## PANEL 1: ORGANIC MATTER—GENERAL

### CONSTITUTION—

C. J. Regan, B.Sc., F.R.I.C.

(Chairman)

G. S. Clements, A.R.C.S., F.R.I.C.

(Secretary)

W. M. Cameron, M.Inst.S.P., F.R.I.C.

W. T. Lockett, M.Sc.

T. B. Moore, B.Sc.

A. E. J. Pettet, B.A.

I. S. Wilson, M.Sc., Ph.D., A.R.I.C.

Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.

Formerly Chemist-in-Chief, London County Council

Public Health Department, London County Council

Main Drainage Department, Middlesex County Council

Formerly of the Main Drainage Department, Middlesex County Council

North Thames Gas Board

D.S.I.R., Water Pollution Research Laboratory

Monsanto Chemicals Ltd.

Secretary to the Analytical Methods Committee

## PANEL 2: METALLIC CONTAMINANTS

### CONSTITUTION—

N. T. Wilkinson, F.R.I.C.

(Chairman)

R. Belcher, Ph.D., D.Sc., F.Inst.F., F.R.I.C.

D. C. Garratt, Ph.D., D.Sc., F.R.I.C.

J. H. Hamence, M.Sc., Ph.D., F.R.I.C.

J. G. Sherratt, B.Sc., F.R.I.C.

Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.

(Secretary)

Imperial Chemical Industries Ltd. (Alkali Division)

University of Birmingham (Department of Chemistry)

Boots Pure Drug Co. Ltd.

Public Analyst, Official Agricultural Analyst and Consulting Chemist

Public Analyst and Consulting Analytical Chemist

Secretary to the Analytical Methods Committee

## PANEL 3: NON-METALLIC CONTAMINANTS

### CONSTITUTION—

F. G. Broughall, B.Sc., F.R.I.C.

(Chairman)

Midland Tar Distillers Ltd.

W. G. Carey, F.R.I.C.

*Public Analyst and Official Agricultural Analyst;  
Consultant*

G. U. Houghton, M.Sc., Ph.D., F.R.I.C.

*South Essex Waterworks Co.*

E. A. W. Whitlock, B.Sc., A.R.I.C.

*Wallace & Tiernan Ltd.*

(Deputy: J. F. Malpas, B.Sc., A.R.I.C.)

## PANEL 4: PHYSICAL TESTS

## CONSTITUTION—

J. G. Sherratt, B.Sc., F.R.I.C.

*Public Analyst and Consulting Analytical Chemist*

(Chairman)

L. Klein, M.Sc., Ph.D., M.Inst.S.P., F.R.I.C.

*Mersey River Board*

G. A. Vaughan, F.R.I.C.

*Coal Tar Research Association*

K. A. Williams, B.Sc., Ph.D., A.Inst.P.

*Analytical and Consulting Chemist*

M.Inst.Pet., F.R.I.C.

Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.

*Secretary to the Analytical Methods Committee*

(Secretary)

## PROGRESS OF WORK—

With the passing of the Rivers (Prevention of Pollution) Act in 1951 it became obvious that there should be accepted methods of analysis available in the event of dispute arising as to the composition of trade effluents. The Federation of British Industries Legislation Committee, therefore, asked the Association of British Chemical Manufacturers to investigate the position and to take the necessary steps to implement the work of approving or devising suitable methods of analysis.

The result of the investigation was the formation of this Joint Committee of the Association and the Society for Analytical Chemistry, with the terms of reference quoted above, and the first meeting was held in March, 1954. In view of the urgent need for recommended methods it was decided that they should be published individually in *The Analyst* as soon as they were deemed satisfactory, rather than waiting until a complete collection had been made. Since this procedure would produce a haphazard collection of methods, it was also decided that they should subsequently be arranged and published as an integrated volume.

Because the existing literature on the analysis of trade effluents was found to be scant, the Joint Committee's task proved to be more arduous than had at first been envisaged and, although the majority of methods that have been recommended are based on existing ones, it was usually found necessary to make modifications to take into account the possibility of interference by a number of substances under very varying conditions. Consequently, it was imperative that before such modified methods could be finally recommended, they should be subjected to check tests by panel members. Some methods, on the other hand, had to be specially devised with a good deal of attendant experimental work.

It is gratifying to report that, after just over 3½ years of unremitting and intensive work by its four panels, the Joint Committee's programme was completed at the end of 1957.

Practically all of the methods have been published in *The Analyst* since January, 1956. The remaining six methods have only just been completed and approved and are being included directly in the book, publication of which is expected before the end of April, 1958. They will, however, also appear in *The Analyst*.

Mention has already been made in the General Review section of this Report of the research that is proceeding under the direction of Dr. Irving to devise a method that is sensitive enough for determining minute traces of silver in the presence of organic matter. It was considered advisable to include a method for silver because of its extreme toxicity to fish, although it is very unlikely that it will be a common contaminant in view of its economic value.

Because many laboratories have to undertake the analysis of sewage effluents as well as trade wastes, cognisance has been taken of the methods recommended by the Ministry of Housing and Local Government in their publication "Methods of Chemical Analysis as Applied to Sewage and Sewage Effluents" (Second Edition, 1956) and, where possible, similar methods (modified as necessary to cover the special requirements for trade effluents) have been recommended. This need for uniformity is especially desirable where empirical methods are used and permission was, therefore, obtained from H.M. Stationery Office for reproduction in full of the methods for the determination of biochemical oxygen demand and of dissolved oxygen.

# REPORT OF THE P.S. - S.A.C. JOINT COMMITTEE ON METHODS OF ASSAY OF CRUDE DRUGS

## MAIN COMMITTEE

### CONSTITUTION—

#### *Representing the Pharmaceutical Society of Great Britain—*

K. R. Capper, Ph.D., B.Pharm., F.P.S., D.I.C.

(Chairman)

R. Higson, F.P.S.

W. Mitchell, B.Sc., Ph.D., F.R.I.C.

R. E. Stuckey, Ph.D., D.Sc., F.P.S., F.R.I.C.

#### *Representing the Society for Analytical Chemistry—*

C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.

H. C. Macfarlane, A.R.T.C.S., F.R.I.C.

D. Watt, F.P.S.

D. C. Garratt, Ph.D., D.Sc., F.R.I.C.

(*ex officio*)

#### *Representing the Tropical Products Institute—*

A. J. Feuill, B.Sc., Ph.D., A.R.I.C.

*Pharmaceutical Society of Great Britain*

*Ministry of Health, Supplies Division*

*Stafford Allen & Sons Ltd.*

*British Drug Houses Ltd.*

*Boots Pure Drug Co. Ltd.*

*Analytical and Consulting Chemist*

*T. & H. Smith Ltd.*

*Chairman of the Analytical Methods Committee*

Miss C. H. Tinker, B.Sc., Ph.D., A.R.I.C.

(Secretary)

*Tropical Products Institute*

TERMS OF REFERENCE—"To prepare standard methods of assay of crude drugs and kindred materials."

### PROGRESS OF WORK—

As mentioned in the General Review section of this Report, this Joint Committee of the Pharmaceutical Society and the Society for Analytical Chemistry was set up in March, 1956. Five working panels have been appointed so far, and the progress of their work is reported individually below. Other panels will be appointed from time to time, when urgent problems present themselves.

## PANEL 1: *Digitalis purpurea*—CHEMICAL METHOD

### CONSTITUTION—

Professor H. Brindle, M.Sc., F.P.S., F.R.I.C.

(Chairman)

G. E. Foster, B.Sc., Ph.D., F.R.I.C.

G. J. Rigby, M.Sc., Dip-Bact.

J. M. Rowson, M.Sc., Ph.D., F.P.S.

K. L. Smith, M.P.S.

Professor J. P. Todd, Ph.D., F.P.S., F.R.I.C.

Miss A. M. Parry, B.Sc.

(Secretary)

*Emeritus Professor of Pharmacy, University of Manchester*

*Wellcome Chemical Works*

*University of Manchester (Department of Pharmacy)*

*Pharmaceutical Society of Great Britain*

*Boots Pure Drug Co. Ltd.*

*Royal College of Science and Technology, Glasgow (School of Pharmacy)*

TERMS OF REFERENCE—"To investigate chemical methods for the assay of digitalis and its preparations and to attempt to correlate them with the biological method of assay."

### PROGRESS OF WORK—

As a preliminary to its work the Panel is comparing the figures for potency of the drug as obtained by standard biological methods with those obtained by chemical methods for the determination of the total active glycosides to find out whether any correlation exists.

Collaborative tests have been carried out on two samples of digitalis leaf, one being a "good" leaf and the other a "poor" leaf (as determined by biological assay). Determinations of the glycoside content by several chemical methods have yielded good agreement between laboratories, but so far these show no correlation with the biological assay. As it appears that several glycosides are responsible for the total activity of the drug, and others are inactive, methods involving chromatographic separation and estimation of the total primary glycosides are now being studied.

It is by no means certain that existing biological methods give a true indication of the potency of the leaf and it is hoped to arrange for information on this point to be obtained from clinical tests, and by comparison of different methods of biological assay.

The Panel is most grateful to Messrs. F. Hoffmann - La Roche & Co. Ltd. A.G. for a gift of 10 g of pure digitoxin to be used as a reference standard at a later stage in the work.

#### PANEL 2: CAPSICUM—CAPSAICIN CONTENT

##### CONSTITUTION—

H. B. Heath, M.B.E., B.Pharm., F.P.S.  
(Chairman)

*Stafford Allen & Sons Ltd.*

E. A. Elsbury, F.R.I.C.

*Parke, Davis & Co. Ltd.*

Miss B. M. Luckett

*W. J. Bush & Co. Ltd.*

C. A. MacDonald, B.Sc., F.R.I.C.

*Evans Biological Institute*

G. R. A. Short, F.P.S.

*W. J. Bush & Co. Ltd.*

D. O. Singleton, B.Sc.

*Beecham Maclean Ltd.*

Miss A. M. Parry, B.Sc.

(Secretary)

TERMS OF REFERENCE—"To investigate methods of assay of capsicum and capsicum products with particular reference to the determination of the capsaicin content."

##### PROGRESS OF WORK—

Several published methods have been critically examined and after an appreciable amount of collaborative work considerable progress has been made towards the establishment of a satisfactory method of determining the capsaicin content of chillies and also of oleoresins prepared from them. This consists in two alternative procedures for the isolation of capsaicin, one chromatographic and the other by alkali extraction, after which the capsaicin content is calculated directly from the extinction value. A confirmatory colorimetric method has, after considerable modification, also been found to be acceptable. It had been hoped that this method would give results sufficiently accurate to quote an extinction value for the coloured capsaicin complex, but this has not proved to be so and it is, therefore, necessary to prepare a standard absorption curve at the same time as the test. The possibility of finding an alternative synthetic standard to avoid constant handling of capsaicin is still under consideration.

Future work will be concerned with the application of the methods to paprika, tinctures and other preparations containing capsaicin.

#### PANEL 3: ANTHRAQUINONE DRUGS

##### CONSTITUTION—

J. M. Rowson, M.Sc., Ph.D., F.P.S.  
(Chairman)

*Pharmaceutical Society of Great Britain*

J. W. Fairbairn, B.Sc., Ph.D., F.P.S., F.L.S.  
F.R.I.C.

*University of London, School of Pharmacy*

C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.

*Boots Pure Drug Co. Ltd.*

W. Mitchell, B.Sc., Ph.D., F.R.I.C.

*Stafford Allen & Sons Ltd.*

H. A. Ryan, B.Sc., F.R.I.C.

*Westminster Laboratories Ltd.*

W. Smith, B.Sc., F.R.I.C.

*Allen & Hanburys Ltd.*

Miss A. M. Parry, B.Sc.

(Secretary)

TERMS OF REFERENCE—"To investigate methods for estimating the purgative activity of drugs and preparations of drugs containing anthraquinone derivatives with a view to recommending standard methods of assay."

##### PROGRESS OF WORK—

Collaborative work is being carried out on samples of both Alexandrian and Tinnevely senna pod and a comparison is being made between the sennosides content found by chemical methods and the activity determined by biological assay.

#### PANEL 4: RAUWOLFIA

##### CONSTITUTION—

C. A. Johnson, B.Sc., B.Pharm., F.P.S., A.R.I.C.  
(Chairman)

*Boots Pure Drug Co. Ltd.*

T. Davies, B.Sc., A.R.I.C.

*CIBA Laboratories Ltd.*

F. G. Farrell, B.Pharm., M.P.S., A.R.I.C.

*Pharmaceutical Society of Great Britain*

J. J. Lewis, M.Sc., F.P.S.

*University of Glasgow (Department of Materia*

*Medica and Therapeutics)*

A. W. Peacock, B.Pharm., F.P.S.

*Riker Laboratories Ltd.*

Miss A. M. Parry, B.Sc.

(Secretary)

TERMS OF REFERENCE—"To investigate methods of assay for rauwolfia and its preparations with particular regard to the content of reserpine and related alkaloids."

PROGRESS OF WORK—

The main problems confronting the Panel in formulating a suitable assay procedure are the considerable number of alkaloids present in rauwolfia as well as the large number of species of rauwolfia in which distribution of the alkaloids varies.

The first year's work has been devoted to the study of *Rauwolfia serpentina*, which is one of the major commercial sources and for which there is a method published in the B.P. Codex, 1954. It has been decided to seek to establish a method indicating the commercial value of the sample as a source of reserpine, rather than to devise a method that would show correlation with the biological activity of the whole root.

Two approaches to the problem have so far been considered, both of which are based on published methods. Good progress is being made in the investigations on one of these, a colorimetric method, which it is hoped may prove suitable for recommendation while investigations into a more specific and fundamental method continue.

Preliminary exploratory work on the ultra-violet absorption characteristics of reserpine and rescinnamine and of the acids produced as decomposition products showed the second method to be basically unsound because of the rapid deterioration of one of the acids when exposed to light. The cause of this deterioration is now being studied and it is hoped that valuable information may emerge regarding the mechanics of the reaction.

The Panel is grateful to Messrs. CIBA Laboratories Ltd. and Messrs. Riker Laboratories Ltd. for generous gifts of samples of pure alkaloids and of *Rauwolfia serpentina* for use in the Panel's work.

PANEL 5: LONCHOCARPUS AND DERRIS

CONSTITUTION—

R. F. Phipers, B.Sc., Ph.D.  
(Chairman)

R. Buckley, B.Sc., A.R.I.C.  
J. A. Dawson, B.Sc., A.R.I.C.

W. E. Drinkwater, F.R.I.C.

R. V. Foster, M.Sc., A.R.I.C.

S. C. Jolly, B.Pharm., B.Sc., F.P.S., A.R.I.C.

J. T. Martin, B.Sc., D.Sc., F.R.I.C.

D. V. Richmond, B.Sc.

W. M. Seaber, B.Sc., F.R.I.C.

F. H. Tresadern

Miss A. M. Parry, B.Sc.

(Secretary)

The Cooper Technical Bureau

Plant Protection Ltd.

Tropical Products Institute

Boots Pure Drug Co. Ltd.

The Cooper Technical Bureau

Pharmaceutical Society of Great Britain

University of Bristol (Long Ashton Research Station)

University of Bristol (Long Ashton Research Station)

Salamon & Seaber

Stafford Allen & Sons Ltd.

TERMS OF REFERENCE—"To investigate methods of assay of derris, lonchocarpus and their preparations, with particular reference to the determination of their rotenone content."

PROGRESS OF WORK—

At the Panel's first meeting in July, 1957, it was agreed that, although methods exist for use in trade transactions in derris and lonchocarpus, the agreement between different analysts' results is unsatisfactory. No collaborative work had been done on the latter, which is now the main material of commerce and there is a need for a reference method for determining the true rotenone content of the sample. Collaborative work on gravimetric methods for the determination of rotenone has begun.

## APPENDIX I

THE SOCIETY FOR ANALYTICAL CHEMISTRY ANALYTICAL METHODS TRUST  
ACCOUNTS FOR THE YEAR ENDED OCTOBER 31ST, 1957*Income and Expenditure Account for the Year Ended October 31st, 1957*

1956		£		1956		£	
£	£			£	£		
	Rent, Light, Heat and				Subscriptions from In-		
630	Telephone .. ..	289			dustry as a result of		
2274	Salaries .. ..	2630			Appeal:		
81	Office Equipment ..	487			Received in 1955 for		
168	Printing and Stationery	184		150	1957 .. ..	150	
62	Travelling Expenses ..	20		6344	Received during 1957	5750	
26	Expenses of Meetings ..	107		6494			5900
21	Audit Fee .. ..	21			Interest from Invest-		
	Postage and Petty Ex-				ments:		
83	penses .. ..	78		7	Received gross ..	7	
3345			3816	2	Received net ..	2	
525	Scholarship Grant ..	958		1	Income Tax re-		
	Excess of Income over			10	coverable .. ..	1	10
	Expenditure for the				Bank Deposit Interest ..		28
	year ended October						
	31st, 1957, transferred						
	to Accumulated Fund		1164				
2634							
<u>£6504</u>		<u>£5938</u>		<u>£6504</u>		<u>£5938</u>	

*Accumulated Fund*

1956		£		1956		£	
£				£			
	Legal Expenses in connection with			6779	Balance at October 31st, 1956 ..	9690	
93	formation of the Trust .. ..	—			Analytical Chemistry Research		
9690	Balance carried to Balance Sheet ..	10,854			Fund—		
				370	Balance at October 31st, 1955		
					transferred .. ..	—	
					Excess of Income over Expenditure		
				2634	for the year ended October 31st,		
					1957 .. ..	1164	
<u>£9783</u>		<u>£10,854</u>		<u>£9783</u>		<u>£10,854</u>	

*Balance Sheet at October 31st, 1957*

1956		£		1956		£	
£				£			
	Accumulated Fund:				Investments (at Cost):		
9690	Balance at 31st October, 1957 ..	10,854			£100 3¼% Ceylon Govern-		
21	Sundry Creditors .. ..	914			ment Stock, 1934-59 ..	61	
150	Subscriptions in Advance .. ..	—		244	£100 3¼% Conversion Stock	83	
					£100 3¼% War Stock ..	100	
					(Market Value at 31.10.57		244
					£203)		
					Sundry Debtors:		
				1	Income Tax recoverable ..	3	
					Interest accrued on Deposit		
					Account .. ..	28	
							31
				9474	Cash at Banks:		
					Deposit Account .. ..	7000	
					Current Account .. ..	4493	
				142	In Hand .. ..		
							11,493
<u>£9861</u>		<u>£11,768</u>		<u>£9861</u>		<u>£11,768</u>	

*Report of the Auditors to the Trustees of The Society for Analytical Chemistry Analytical Methods Trust Fund*

We have examined the above Balance Sheet which in our opinion gives a true and fair view of the state of affairs of the Trust at 31st October, 1957.

10 New Court,  
Lincoln's Inn,  
LONDON, W.C.2.  
4th March, 1958.

(Signed) RIDLEY, HESLOP & SAINER,  
*Chartered Accountants,  
Auditors.*

*Schedule of Investments at October 31st, 1957*

	Nominal Amount	Cost	Market Value 31.10.57	Income Received Gross
Ceylon Government 3½% Stock, 1959 .. .. .	100	61	79	3
3½% Conversion Stock .. .. .	100	83	63	4
3½% War Stock .. .. .	100	100	61	3
		<u>£244</u>	<u>£203</u>	<u>£10</u>

## APPENDIX II

### SUBSCRIBERS TO THE TRUST FUND DURING 1957

Albright & Wilson Ltd.	Imperial Chemical Industries Ltd.
The Associated Ethyl Company Ltd.	Laporte Chemicals Ltd.
Bakelite Ltd.	J. Lyons & Co. Ltd.
Baker Perkins Ltd.	Macfarlane, Lang & Co. Ltd.
J. Bibby & Sons Ltd.	John Mackintosh & Sons Ltd.
A. Boake, Roberts & Co. Ltd.	Marmite Ltd.
Boots Pure Drug Co. Ltd.	May & Baker Ltd.
Borax Consolidated Ltd.	The Metal Box Company Ltd.
The British Aluminium Co. Ltd.	The Millers' Mutual Association
The British Arkady Co. Ltd.	Monsanto Chemicals Ltd.
British Celanese Ltd.	Oxo Ltd.
The British Drug Houses Ltd.	Peek, Frean & Co. Ltd.
British Glues & Chemicals Ltd.	Procea Products Ltd.
Brotherton & Co. Ltd.	Reckitt & Colman Ltd.
Cadbury Brothers Ltd.	Research Laboratories, General Electric Co. Ltd.
Central Electricity Authority	Rowntree & Co. Ltd.
The Distillers Company Ltd.	"Shell" Research Ltd.
Dunlop Research Centre	Stafford Allen & Sons, Ltd.
Esso Development Co. Ltd.	John & E. Sturge Ltd.
Ferranti Ltd.	Tate & Lyle Ltd.
Fisons Ltd.	Unilever Ltd.
Glaxo Laboratories Ltd.	Vitamins Ltd.
Arthur Guinness, Son & Co. (Park Royal) Ltd.	Weston Research Laboratories Ltd. (formerly Allied Bakeries Research Laboratories Ltd.)
H. J. Heinz Ltd.	
Hopkin & Williams Ltd.	
Huntley & Palmers Ltd.	

# The Fifth Bernard Dyer Memorial Lecture

## Science and Politics

By SIR HUGH LINSTEAD, O.B.E., LL.D., F.P.S., M.P.

*(Delivered after the Annual General Meeting of the Society, February 26th, 1958)*

To be asked to give the fifth Bernard Dyer Memorial Lecture is an honour I greatly appreciate. The purpose of the lecture is primarily to do honour to the memory of the life and work of Bernard Dyer, one of the founders of this Society. As the years pass the number of those who knew him will become smaller and there will be fewer additions to be made to the known details of his life. It is therefore fortunate that in the first lecture Sir John Russell recorded so living a picture of him, from which he emerges as one of the great individualists of the period when chemistry in this country was taking shape as an organised profession.

Such links as I can claim with him are through the Pharmaceutical Society, where he studied in the laboratory that had once been Hofman's, and through the City of London School. Here, incredibly, he was taught chemistry in 1871 by the same Isaac Scarf who taught me in 1914, forty-three years later. I met him personally once only, but he remains in my memory as a twin figure with that other individualist of the same epoch, Henry Armstrong. There are fewer such men to-day and we are the poorer.

The two main interests in my life have been pharmacy and politics and I have chosen as the title of this lecture "Science and Politics." I want in it to discuss the relation between those two disciplines and, if I can, to define the place that the scientist has to fill in politics.

It will be useful first of all to look at examples of the sort of scientific problems that impinge most closely on politics. These are problems about which the scientist is equipped to speak authoritatively and yet he often finds that his answer is not the final one. If one were to list those likely to have the most profound effect upon humanity during the next century they would fall into two rough groups. There are the old biological problems that have been with mankind throughout its struggling history—the relation between populations and foodstuffs; the preservation of natural resources; the conservation and utilisation of water supplies. And then there are those more recent challenges that at present outstrip our ability to regulate them—nuclear fission; penetration into outer space; and all that is implied in the term "brain-washing."

Each one of these, the old and the new, represents a field in which science and politics are inextricably mixed and to which both scientist and politician have contributions to make, although differing both in form and in content. In reviewing these problems the scientist's approach is simple and direct. The politician's, for valid reasons that will appear in due course, hesitating, fumbling, circumambulant. I speak here of the politician in a parliamentary democracy. The scientist's method is inductive: here are the facts, where do they lead me? The politician proceeds deductively: there is the goal, how do I get to it? But they are fundamentally different in so far as there always intrudes into the political approach the incalculable element of the reactions of human beings.

One or two examples will illustrate this.

Sir Harold Hartley, in the first Graham Clark Memorial Lecture before the Institution of Civil Engineers in May, 1955, thus sums up the achievement of the Tennessee Valley scheme with its 27 dams and reservoirs controlling a river basin of 40,000 square miles:

"The reservoirs provide 11½ million acre-feet of storage for flood control at the beginning of the flood season and have saved an immense amount of flood damage each year. Six million acres of rich bottomland is protected in this way. The replanting of the slopes has stopped soil erosion, has made the muddy streams clear again and delayed the silting of the reservoirs. T.V.A. brought new life into a depressed area and did much to raise its standard of living."

This is an objective scientific assessment of the benefits that have (almost literally) flowed from this great federal project. That was what the scientists promised and what they gave to the community. Yet what were the political reactions that it provoked? Opposition from the outset that was none the less fierce because at that period of agonising depression in the American economy it had to be under cover. And opposition subsequently

with the objective that there should never again be such a dynamic use of combined national resources unless indeed the country were to be driven to initiate public works by reason of a comparable slump to that of 1930.

Why this political opposition to a great economic achievement? It was not simply that private vested interests moved in again once the emergency was past. Opposition to Roosevelt's New Deal was based upon deep conviction. If we remove the same problem to another comparable area, the Danube Basin, we find F. A. Hayek in "The Road to Serfdom" maintaining that "one cannot create a kind of Tennessee Valley Authority for the Danube Basin without thereby determining beforehand for many years to come the relative rate of progress of the different races inhabiting this area, or without subordinating all their individual aspirations or wishes to this task. . . . Though there are no doubt many people who honestly believe that if they were allowed to handle the job they would be able to settle all these problems justly and impartially, and who would be genuinely surprised to find suspicion and hatred turning against them, they would probably be the first to apply force when those whom they mean to benefit prove recalcitrant, and to show themselves quite ruthless in coercing people in what is presumed to be their own interests."

You may feel that a Macedonian or Bulgarian peasant would willingly sacrifice some modicum of such liberty as poverty allots to him in return for a plentiful supply of water and power. You may feel that the choice in such cases often lies between collective action and no action at all and that Hayek's arguments have no roots in reality. Nevertheless, they represent political ideals deeply and sincerely held. They have no relevance to the scientific balance sheet of schemes such as the T.V.A. or the Danube Basin: that balance is measured in gallons and kilowatts. But a politician can ignore ideals such as Hayek's only at his peril.

A neat example of the interplay of politics and scientific irrigation schemes is mentioned in "Report of the Royal Commission on East Africa" (Cmd. 9475 of 1955). The Commission point out that "throughout East Africa the lack of discovered or developed water supplies is a major factor in preventing the use of otherwise productive resources." They recognise that some part of the limited finance of the governments of the East African territories should be devoted to meeting this basic need. What could be more straightforwardly obvious than that this money should be used on schemes selected by the Government for priority? But the Commission warn against such utilisation of government water-development agencies operating at or below cost. Experience in Kenya has shown that once government shows itself prepared to move into this field and offer its services on what are in effect subsidised terms, numbers of farmers forthwith postpone embarking on water development privately and wait for their turn in the government scheme. The result is likely to be that the amount of water development may prove to be less than if the government had never moved in at all! . . . But perhaps this is not politics but simply human nature!

The reverse process—politics driving science—is vividly illustrated in Israel. The Proclamation setting up the new State of Israel in 1948 declared that Israel "will be open to the immigration of Jews from all countries of their dispersion." No Jew who reached Israel could be turned away, and since mid-1948 nearly 900,000 Jewish immigrants have been received. The total population, Jews, non-Jews and immigrants, at the end of 1956 was about 1,800,000. So in ten years the population had doubled. Politically, that meant that every natural resource of the country had to be developed vigorously. Scientifically, that largely meant the development of water resources.

From Dan to Beersheba the country is green. From Beersheba to Eilat on the Red Sea there is brown desert, the Negev. You fly south from Tel-Aviv over a landscape of the moon. Through this the Israelis have driven a monumental motor road and at rare intervals in this barren desolation groups of bungalows can be picked out, each with its minute miracle of green where the desert is being compelled to flower.

Israel's irrigated area has increased from 300,000 dunams in 1948-49 to 1,000,000 in 1955-56. (A dunam is a quarter of an acre.) These achievements are spectacular, and one cannot but observe the almost complete absence of similar initiative by Egypt in Sinai and the Gaza strip and by Jordan along her long frontier with Israel. As I have said, political necessity has forced irrigation on Israel. But even there politics has at the same time compelled a truncated scheme. There can be no region where a comprehensive water conservation scheme would be more rewarding than in the whole of this part of the Middle East. It should include Lebanon and Syria in the north, Israel and Jordan in the centre and Egypt

and Saudi Arabia in the south. But one has no sooner named the countries concerned than politics rears its head. The feud between Arab and Jew is paralleled only by that between Muslim and Hindu, and makes any large scale co-operative enterprise a matter of immense difficulty even were the atmosphere not darkened by the aftermath of the Sinai campaign.

These examples could be multiplied many times to show how politics blunts the edge of science. Take another of these fundamental biological problems where science and politics interlock—the reactions between population and food supply. The name linked with the first discussion of this problem in our own country and our own times is, of course, that of the Rev. Thomas Robert Malthus, curate of Albury in Surrey, who, in 1798, published his "Essay on the Principle of Population." He argued that population would soon increase beyond the means of subsistence and that checks on this increase are necessary. The essay aroused a storm of controversy and, in his second edition in 1803, Malthus modified some of his conclusions.

The problem remains a cardinal one in Africa and in Asia to-day. There are still some who accept the Malthusian doctrine. But the better view seems now to be that an increase in population provides by its own labour the food and other resources it needs. It is a problem of fundamental importance for the European settlers in Africa. They are, of course, fearful of the consequences of a steady increase of the African population and this fear evidently coloured their evidence to the Royal Commission to which I have already referred, evidence that seems to have been based on the belief that the Africans were increasing at an annual rate of 2 per cent. and would double their numbers in thirty-five years.

To what was essentially a political approach the Commission opposed a scientific one. They undertook a statistical examination of the available census figures and reported that "apprehensions concerning an unduly rapid rate of population growth are not supported by the statistical material available; there is no evidence that the African population as a whole is increasing at an annual rate of 2 per cent.; [although] there has been an upward movement in the rate of natural increase."

But although science speaks here with an authoritative voice and has figures on its side, no politician would be so simple as to imagine that that disposes of the affair. The fear of the European that he will some day be drowned in a sea of Africans is too deeply planted to be eradicated by statistics, however authoritative.

As examples of ways in which politics and science may interact, I have chosen two—conservation of water and the relation between population and food—where science may claim to be on the side of the angels, wherever that may leave politics. I want by way of contrast to take an example where science, unless it shows high responsibility, can all too easily serve the devil. It is what we to-day crudely call "brain-washing," and it takes us back to Pavlov and his dogs.

Pavlov knew that when a hungry dog saw food it would salivate. A bell was rung at the same time as he fed his dogs and he found, after many repetitions, that they would salivate at the sound of the bell even in the absence of food. From this Pavlov developed the theory of the conditioned reflex, which explains learning as the building up in the individual of a jig-saw of conditioned reflexes each one based on a different stimulus. It is this process, recognised for half a century and mildly applied in such persuasive operations as advertising, that has now been conscripted into the service of Soviet Russia.

Dr. Joost Meerloo, formerly Chief of the Psychological Department of the Dutch armed forces and now of Columbia University, New York, describes two institutions, part of the Moscow Academy of Science, that are dedicated to the political application of the Pavlov theory. He says, "They are under orders to emphasise the purely mechanical aspects of Pavlov's findings. Such a theoretical view can reduce all human emotions to a simple, mechanistic system of conditioned reflexes. Both organisations are control agencies dealing with research problems and the scientists who work on them explore the ways in which man can theoretically be conditioned and trained as animals are."

Now it so happens that in this current month, *Express*, a French weekly, has been publishing (January 31st, February 6th and February 13th) an account of the experiences of a Hungarian, Lajos Ruff, aged 26, during his "brain-washing" by the political police in Buda-Pest for six weeks until he was released during the abortive revolution of October, 1956. It reads like a fairy story and Ruff may be the only witness available to testify to its truth. And yet I have a firm feeling that his tale is in the main true. The headquarters of the political police in Buda-Pest, Andrassy-utca 60, had an unsavoury reputation when I was

there in 1947. I can remember also all too well an unhappy woman who came to see me at the Bristol Hotel with a tale of the condition in which she found her husband when she was allowed to visit him. There was again the experience of the father of a Hungarian friend of mine now in England, who was frequently visited by the political police at all hours of the day or night, taken away to the commandatura and detained there, ostensibly for interrogation but in fact to break his spirit. And then there is Cardinal Mindszenty. I had the privilege of spending a full day with him at Esztergom and I subsequently read the verbatim account of his trial. The Mindszenty who gave evidence at the trial was no longer the Mindszenty of Esztergom.

And so I am prepared to believe the substance of what Ruff has to say. This, remember, is not the Arabian Nights. It is Europe in 1956.

He was confined in a comfortable cell, which he soon began to visualise as "the magic room," where one was free from all responsibility for decisions of any kind. Here he was first conditioned to mistrust himself. He was put to sleep. When he was woken up a kindly doctor would accuse him of attempted suicide. He would deny it only to find a cut artery banded up and blood on the floor. Or he would be accused of trying to strangle himself. A scarf would be found in his bed and his neck would be severely bruised.

Then he was conditioned to believe that he could never escape. A ray of light was projected into his cell. He was told to keep away from it as it would damage him. But wherever he stood or sat or lay it crept slowly towards him. Finally after some days he was convinced he could not escape it and so he flung himself into it, only to find it harmless and to sink into an exhausted sleep.

He was given perpetual cinema shows so that finally the frontiers between the real and the imaginary lost their significance. "I cut myself off from real life," he says, "I had no decisions to make. I had no need to think. . . ." Even when the door of his cell was left open, he had no desire to escape.

It was at this stage that he began to reveal the names of friends. It had ceased to be a matter of any reality or meaning to him that they existed or what might happen to them as the result of his disclosures.

One final quotation—

"To the extent that I lost confidence in myself, my confidence in the doctor increased. . . . I was not far from the state in which one is said to say no matter what to a tribunal which seems to you unreal so that you can get back more quickly to the sole reality that matters, the safe world of the magic room."

Well, there it is: civilisation in the year of Our Lord 1956. Scientists may say hard things at times about politicians. Let them reflect with some humility on this prostitution of science by scientists as well as by politicians.

I want to take briefly one other example of a field where politics and science interlock all too closely. That is the field of nuclear energy. There is no need to go over the familiar arguments in detail—the immense potential benefits to mankind and the immense dangers. What is of interest for our argument is that you have here a fundamental scientific discovery that has been hurled into the political arena and become the centre of acute controversy. Members of Parliament are willy-nilly having to equip themselves with all the vocabulary of atomic science and the Prime Minister is rapidly qualifying himself for a senior teaching post in a university department of nuclear physics. It is right that there should be this intense concern. What, however, is less laudable is the manner in which scientific facts have become twisted and distorted to provide material for purely party debates. We know that there are dangers from radioactive fall-out. We do not know accurately what those dangers may be. In such circumstances it is surely not for responsible persons to exaggerate those dangers without information and to alarm the community by partisan statements. What is needed is the fullest information from the most reliable sources to enable some judgment to be formed of how far the danger extends and what are the risks we are running. That course was eventually followed and an almost historic report on the hazards of radioactive fall-out was brought out by a committee of the Medical Research Council under the chairmanship of Sir Harold Himsworth. But not before harm had been done by the irresponsible use of partial and distorted information for political purposes.

I am not concerned to-night to defend or attack the two-party system as it has developed in this country. It has much to be said in its favour. Many of my French friends—some of them experienced members of the Assemblée Nationale—speak enviously of the strength that the system

ensures for the government of the day. And I am certainly no advocate of a multi-party system nor of that will-o'-the-wisp a national government of coalition. But I must acknowledge that with its many advantages the two-party system has one grave disadvantage. According to it, the duty of the Government is to govern and the duty of the Opposition is to oppose. And that latter duty can be in some circumstances interpreted to justify the use of almost any means to embarrass or discredit the Government. Both the parties are open equally to this criticism. At times when feeling is running high it is all too easy for partisanship to outrun discretion and responsibility. It is such occasions—perhaps they occur too often—that get politics and the politician a bad name, particularly when it is possible to compare side by side the reactions to the same problem among scientists and among politicians. Yet, broadly speaking, I am here to defend the politician in spite of actions that may from time to time appear to be indefensible in his behaviour or his decisions.

Politics, in its parliamentary context, has been defined as "the infinite adventure of governing men." A French professor to whom I shall refer again, Gustav Le Bon, once wrote that governing men is a very difficult matter and that the most a statesman can hope to achieve is "not to be too much governed by them." Be that as it may, someone must attempt to govern and in a parliamentary democracy this implies the consent of the governed and therefore that he who governs shall conform to the only conditions—however distasteful to him—that may permit him to do so. He must "carry the people with him."

Before the United States could be brought into the second World War, the President had slowly to ripen public opinion over two years. One of the major factors in the failure of the Suez operation was the impossibility, for security reasons, of taking any preliminary steps at all to prepare public opinion in this country for such drastic action by our forces. Instead of being prepared, the public was stunned.

Politics is not mathematics. There may be the clearest of reasons for some line of action that can be demonstrated scientifically and yet it may be politically entirely unrealistic. The economic advantages of a union between the two parts of Ireland are no doubt very great. Yet he would be a brave man who would dare even to suggest at a public meeting in Ballymena or Portrush that they might conceivably be worth discussion. I do not doubt that it can be persuasively shown that Israel is not a viable economic unit. But I have equally no doubt that nothing short of physical extinction will prevent that country from developing and improving its living standards steadily. There it is not mathematics that provides the answer. It is will power.

The politician must, of course, use science. But ultimately his decisions are taken by that sixth sense, *le sens du possible*, the sum of all the factors, material, human and moral that bear on a situation.

To underline the cardinal necessity of always carrying the people with you in any major political change may suggest that a Member of Parliament should be merely the delegate of his electors. But this ought never to be so. Edmund Burke stated memorably the relationship between a Member of Parliament and his constituents in his speech to the electors of Bristol after the declaration of the poll on November 3rd, 1774.

"Certainly, gentlemen," he said, "it ought to be the happiness and glory of a representative to live in the strictest union, the closest correspondence, and the most unreserved communication with his constituents. Their wishes ought to have great weight with him; their opinions high respect; their business unremitted attention. . . . But his unbiased opinion, his mature judgment, his enlightened conscience, he ought not to sacrifice to you, or to any set of men living. These he does not derive from your pleasure; no, nor from the Law and the constitution. They are a trust from Providence, for the abuse of which he is deeply answerable. Your representative owes you, not his industry alone, but his judgment; and he betrays, instead of serving you, if he sacrifices it to your opinion."

Nevertheless, the greatest and most independent of statesmen is never a completely free agent to do precisely what he believes should be done at the time when he believes it should be done. He must temper his actions by regarding the state of public opinion. Roosevelt knew it; Baldwin found it out; it was tragically brought home to Sir Anthony Eden.

Gustav Le Bon, to whom I have referred, wrote at the end of the last century a remarkable book, which is too little known. He called it "*La Psychologie des Foules*." It is available in English as "*The Crowd*." By reference mainly to French examples, he attempts an analysis of the motives and ways of behaviour of men and women when they lose their identities as the result of becoming, however temporarily, members of a crowd. "There is

nothing so queer as folk" and Le Bon lays bare the peculiar queerness of folk in the mass. Writing more than sixty years ago, he draws attention to the destruction of the religious, political and social beliefs in which all the elements of our civilisation are rooted. "The ideas of the past," he says, "although half destroyed, being still very powerful, and the ideas which are to replace them being still in process of formation, the modern age represents a period of transition and anarchy. . . . The entry of the popular classes into political life—that is to say, in reality, their progressive transformation into governing classes—is one of the most striking characteristics of our epoch of transition."

Then, by way of an analysis of the characteristics of what he calls a psychological crowd—a crowd in which the individual has come to surrender his personality—he explains the effect on politics and government of this shift in the balance of power from the traditional governing classes to the new governing classes.

From this Le Bon demonstrates that crowds are not to be influenced by reasoning. They think in images and are specially impressed by the marvellous. Among their characteristics he notes impulsiveness, irritability and the absence of judgment and of the critical spirit. This being the condition of human beings when they are assembled in the particular kind of crowd that we recognise as a nation or other political community, he goes on to show that the art of governing them cannot be based primarily on appealing to their reason. For good or for bad, says Le Bon, crowds are led by affirmation without proof, by repetition and by contagion. "To know the art of impressing the imagination of crowds is to know at the same time the art of governing them." "All the great statesmen of every age and every country, including the most absolute despots, have regarded the popular imagination as the basis of their power, and they have never attempted to govern in opposition to it. 'It was by becoming a Catholic,' said Napoleon to the Council of State, 'that I terminated the Vendéen war, by becoming an Ultramontane that I won over the Italian priests, and had I to govern a nation of Jews I would rebuild Solomon's temple.'" And a final quotation: "A knowledge of the psychology of crowds," says Le Bon, "is to-day the last resource of the statesman who wishes, not to govern them—that is becoming a very difficult matter—but at any rate not to be too much governed by them."

The developments studied by Le Bon were reviewed in 1927 by another Frenchman, Julien Benda, in a book he called "*La Trahison des Clercs*"—"Betrayed by the Intellectuals," we might translate it. It was a book that did not attain fame until it was reprinted in 1947 at the end of the second World War. Benda's conclusion—that humanity had been let down by those who should have been its intellectual saviours—seemed to have been tragically reinforced by the behaviour of many of the leaders of French thought during 1939 and 1940 and especially during the German occupation. In his book Benda proclaimed the duty of the intellectuals in every community to be to defend eternal and objective values—reason, for example, and justice.

Surveying the development of humanity from the same viewpoint as Le Bon, Benda suggests that there was a time when human beings could be regarded as forming two groups. There was the mass of the people held together by such forces as membership of the same country or of the same class. And there was the small intellectual class or corporation, which understood and opposed the inadequacy and parochialism of such a limited conception of human association. These latter were the teachers, the artists, the philosophers who were seeking to discover the soul of Europe, something that would rise above nationality. Among other means to their ends they were developing a universal language—Latin—and standards of thought and behaviour based upon the teachings of the Greeks and of Christ. Benda considered that by the time he was writing this corporation of the élite had sold out to the masses. It no longer opposed their purely realistic and material ideas. Indeed, it had taken them over and glorified them. "To-day," he says, "the game is over. The layman has won. . . . Indeed, all humanity has become lay, including the intellectuals." By "lay" he means materialistic and it is this surrender to the whims of the masses that leads him to accuse the intellectuals of *trahison*—treachery, betrayal.

It is the writers—especially the journalists—who come under Benda's lash. The scientist escapes. He escapes largely because he has so far been uncommitted. But the scientist has all the same been increasingly sensitive to his lack of authority in the political application of his discoveries and there is an increasing demand among scientists that they shall have an effective voice in the practical conduct of political affairs. They are, in fact, poised for the decisive move from the objective field of science to the subjective field of politics. And

I want to-night to raise at least one voice against what may well be a tragic decision if it were acted upon by any large group of scientists. In to-day's world—a world of propaganda, cold war, mass hypnotism by broadcasting and by newspapers with vast circulations—truth is too easily a casualty. If humanity is to be deprived of objective standards because the scientist has come down from his uncommitted heights to take sides in the party-political battle, then humanity will be immeasurably the poorer.

To say that the scientist should stand aloof from the party-political contest is not to exclude him from politics in its fullest and best sense. Far from it. He has political duties of the first importance that no one else can perform. The first is to ensure that his discoveries are clearly presented to the public. There is an eager audience waiting to be informed about the significance of scientific developments. There is an immense diversity of means whereby these things can be brought to the eyes and ears of the men, women and children who want to know about them. But just because these means are so potent and so pervasive there is a great responsibility upon those who control them and use them to ensure that, so far as is humanly possible, they are used in the service only of truth as that is understood by science.

This responsibility rests with particular weight on the shoulders of some individuals. The scientific correspondents of great newspapers, those who have the direction of scientific programmes on the radio, those who teach science in schools and universities, cannot escape from it. A special duty rests upon some of our scientific bodies both in specialised fields and generally. The British Association for the Advancement of Science has for long recognised the need in this field and has recently studied ways by which, at its annual meetings and otherwise, it can disseminate still more widely a knowledge of the contributions science is making to human progress.

The interpretation of science to laymen is no easy task. It grows harder as science expands and deepens. It faces the peculiar difficulty that the mass of people, as Le Bon so clearly showed, are neither able to follow a reasoned argument nor wish to do so. They think in images and are at the mercy of someone who can put persuasively and vividly his story to them. This, then, emphasises the need for, and the heavy responsibility of, scientists who are willing to assume the rôle of interpreters of science to the public. They can influence public opinion for good or for bad by a single broadcast or a single newspaper article. To achieve their purpose they must present what they have to say in vivid images and stir the emotions. And yet in selecting their examples and in planning the emphasis of their argument they must regulate themselves by the coldest objective standards. To interpret science to the public is in such circumstances an undertaking of the highest trust and responsibility, worthy of the attention of the finest scientific brains we have.

Within this large field of making science understandable by the public is a narrower field, and the need for it to be adequately filled has been most vividly brought home to me during a now long experience of politics. The politician, and I include the statesman and all who have the direction and decision in affairs of government, is frequently faced with problems the solution to which depends upon an assessment of abstruse scientific facts or probabilities. As we know, the politician is rarely himself equipped to undertake this assessment. For example, what minister is there who from his own knowledge of atomic science or of biology can provide the current answers of science to the questions provoked by the threat of the hydrogen bomb? He must turn to some authoritative scientific source of information. Where is he to find it? It must not only be reliable, it must be shorn of the suspicion of party-political affiliation. Where is he to find it, particularly if science has so involved itself with party politics that individual scientists have aligned themselves with political parties and their opinions have thereby become—rightly or wrongly—suspect and liable to be discounted accordingly? Just as historically the political bishop came to be treated with reserve, so, too, the political scientist handicaps himself and renders less effective his services both to politics and to science.

An historic example of the force with which a completely objective case can be presented for a scientific purpose is Sir Henry Dale's letter to *The Times* on August 8th, 1945, a few days after the first atom bomb had been dropped. He discusses the claims of scientific freedom as opposed to the secrecy imposed by considerations of security.

"This achievement [nuclear fission]," wrote Sir Henry, "at all stages, has been the greatest of war secrets, kept with a magnificent loyalty. The scientists concerned will remain loyal to that duty, guarding closely whatever has still to be kept secret till the war with Japan

is finished. Then, I believe, they will wish to be done with it forever. We have tolerated much, and would tolerate anything, to ensure the victory for freedom; but when the victory is won we shall want the freedom."

Another example, on a different plane, but in its own way intensely stimulating, is the paper read by Sir Charles Goodeve before the South Wales Institute of Engineers at their Centenary Meeting on October 29th, 1957. He called it "The Development of Britain's Physical and Geographical Advantages." He shows how unevenly Britain has developed her advantages and how in fields where there is little or no direct competition the utilisation of our coal and water, for example, we have lagged seriously behind others. He shows a clear appreciation of how politics can bedevil the application of science to improving our affairs.

"We are slow," he says, "to apply modern knowledge because to do this means change and change means hurting a few and benefitting others, generally many others. Those who are about to be hurt scream loudly; those who will benefit keep quiet for fear that they become a target for the screams of the first group. Change leads to opposition and as a consequence a large part of our scientific effort remains unused."

But this does not prevent him from advocating the remedy that, as a scientist surveying our problems objectively against the background of intense scientific development everywhere, he regards as essential—capital investment in modernising industry and its services. And he does this boldly, although recognising that "the vast majority of people will vote for subsidised housing, free medicines, old age pensions, etc., without being conscious of the consequences. This country needs investment more than anything else, but this can only be achieved at the expense of current consumption, the curbing of which is apparently politically impossible."

I am personally not prepared to believe that even this need be politically impossible if science will only tell the community persuasively and clearly what science knows, and I have put these two examples to you to emphasise the sort of rôle that science can fill and that the country badly needs science to fulfil.

A most effective instrument for developing an association between politics and science on a non-party and objective basis is the Parliamentary and Scientific Committee. This consists of some two hundred members of both Houses of Parliament and of all parties, together with representatives of a large number of professional scientific bodies. It forms a bridge between science and politics, enabling members of Parliament to listen to the views of experts on scientific problems that have a bearing on the country's development and enabling scientists to make contact through the members of Parliament with ministers and others who are responsible for the country's educational, scientific and economic progress.

Let me now try to sum up the argument to which you have listened so patiently.

I have been urging that in politics as it is generally understood, that is the rough and tumble of the party-political arena, there is really no appropriate place for the scientist. I am urging him to be the referee, not the player. There can be no socialist physics nor conservative biology: life peerages may remove even heredity from the Upper Chamber. But in the full field of politics, embracing the whole life of the community, the scientist has a part to play of still almost unsuspected importance. He must be not only the discoverer of new things, but also the interpreter of them. He has not only the right, he has the duty to offer advice according to the highest standards of scientific objectivity.

All too often the scientist writes off the politician as someone before whom scientific pearls are cast in vain because he is too concerned with what is popular to busy himself with what is right. In so far as that is true, it underlines this duty that lies on the scientist to interpret his beliefs to those who have the practical duty of applying scientific discoveries to daily affairs. And in so far as it is true that, as a condition of governing at all, the politician must carry the man in the street with him, then the second imperative duty for the scientist who would exercise authority in public affairs is the selling of his discoveries and all they mean to the public. He will have no difficulty in attracting a crowd once he sets up his stall. They are hungry to buy. His problem will arise because so often what he has to sell is so much less than they ask. Science has given to the man in the street so many miracles that he has become insatiable. And he will not believe the scientist who may modestly protest that he does not know, that only time will show or that experiments are inconclusive. Nevertheless, the responsibility is squarely on the scientist's shoulders to help out the politician by revealing to the man in the street the meaning of new discoveries, their limitations and, above all, their more uncomfortable, unpopular or even disastrous implications. And all

that must be done in the passionate images which alone will attract and hold attention, yet must at the same time be illuminated solely by the cold, objective light of scientific truth.

Much of what I have been saying is well summed up in a private note written by Lord Halsbury, which he has kindly said I may quote to you—

"The responsibilities of scientists for the moral consequences of their work must be shared with the community. Any discovery can be put to good or evil use. It does not appear to me that scientists can do more as scientists than explain as clearly as possible to the rest of the community where the possibilities for evil latent in any of their discoveries really lie. The issue is, therefore, whether they do this effectively or ineffectively. I believe scientists would do this more effectively if they could speak on political issues with more authority. I believe this authority would come best from the exercise of a self-denying ordinance in political matters, namely by dissociating themselves from any political party whatever and behaving as public servants are expected to behave."

He goes on to say that this is by no means a negligible request to make of them, since many have sincere and strongly held views. But the things they lose are more than compensated for by the contribution that they make to the moral store of humanity. Sir Henry Dale said at the end of the letter from which I have quoted, "The true spirit of science working in freedom, seeking the truth only and fearing only falsehood and concealment, offers its lofty and austere contribution to man's moral equipment, which the world cannot afford to lose or to diminish."

Julien Benda challenges the scientist as much as any other of the intellectuals. He reminds us that there are certain fundamental standards and truths, represented in the field with which we are more particularly concerned by the objectivity of science, which are in grave danger in this present age. He maintains that it is the duty of the intellectual to protect those standards at all costs. And he then goes further and asserts that if he is to perform that duty the intellectual must keep himself clear of the compromises and temptations of the world of politics. Only so, he asserts, can the truths which so quickly become casualties in the buffetings of everyday existence be kept untarnished. Though the intellectual himself may be crucified, says Benda, yet his words will haunt the memory of men: that is to say, the truths will go marching on until at length they prevail.

## The Spectrophotometric Determination of Parathion and *p*-Nitrophenol

By ELSA HJELT AND ANNA-LIISA MUKULA

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Equal amounts of sample are heated in aqueous alkaline and in alkaline benzene solutions. In benzene solution, no hydrolysis of parathion occurs. The products are extracted with a (1 + 4) mixture of benzene and acetone, which dissolves both parathion and *p*-nitrophenol. The absorption of these solutions is measured over the wavelength range of 400 to 430 mμ. In this region *p*-nitrophenol has a well defined absorption peak and parathion shows no absorption. The absorption of the unhydrolysed solution measures the background absorption from absorbing substances other than parathion. By subtracting this background absorption from that of the hydrolysed sample, the absorption of *p*-nitrophenol formed by hydrolysis of parathion is measured. The ultra-violet spectrum of the sample in 94 per cent. ethanol is also measured, and *p*-nitrophenol is identified before and after hydrolysis by paper-chromatographic methods.

PARATHION (diethyl *p*-nitrophenyl phosphorothionate) is a commonly used insecticide. It is volatile in steam, sparingly soluble in water and soluble in most organic solvents, *e.g.*, benzene<sup>1</sup> and light petroleum.<sup>2</sup> When parathion is heated with alkali it is hydrolysed and the products include *p*-nitrophenol. The analytical methods for the identification and determination of parathion include: paper-chromatographic methods<sup>3,4,5</sup>; methods based on the reactions of the aromatic nitro group<sup>6,7,8,9</sup>; the spectrophotometric determination of parathion<sup>5,10,11,12,13</sup>; and, above all, methods based on the determination of *p*-nitrophenol.<sup>1,13,14,15,16,17,18,19,20</sup>

In some of the methods in which the identification and determination of parathion is based on the measurement of the absorption of parathion itself and that of *p*-nitrophenol after hydrolysis, the results are erroneous. For example, some commercial preparations of parathion contain impurities, such as *p*-nitrophenol and emulsifying agents, which cause background absorption and thus affect the accuracy of the determination.<sup>1,11</sup> These impurities must either be removed or compensation must be made for the background absorption caused by them.

We have observed that the alkali salts of *p*-nitrophenol can be extracted from strong alkaline solutions with a mixture of benzene and acetone, and that the presence of benzene prevents hydrolysis of parathion. These facts, as well as the characteristic absorption in the ultra-violet region exhibited by parathion in ethanolic solution, and by *p*-nitrophenol in alkaline benzene - acetone solution in the visible region, make possible the determination of both *p*-nitrophenol and parathion, and also the measurement of the amount of background absorption in the visible region. The absorption spectra of *p*-nitrophenol and parathion are shown in Fig. 1.

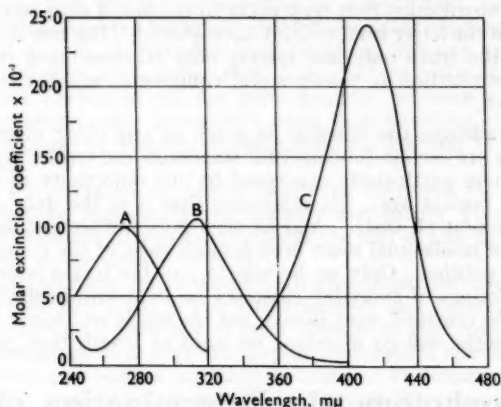


Fig. 1. Absorption spectra: curve A, parathion in 94 per cent. ethanol; curve B, *p*-nitrophenol in 94 per cent. ethanol; curve C, *p*-nitrophenol in alkaline benzene - acetone solution

It can be seen that both *p*-nitrophenol and parathion have absorption peaks in the ultra-violet region. In the visible region, *p*-nitrophenol has a well defined peak, whereas parathion shows no absorption. Beer's law is obeyed over the concentration range used. The wavelength ranges used were from 235 to 320  $m\mu$  and from 400 to 430  $m\mu$ . In 94 per cent. ethanol the absorption peak of parathion occurs at 274  $m\mu$ , and that of *p*-nitrophenol at 315  $m\mu$ . The absorption peak of *p*-nitrophenol in alkaline benzene - acetone solution varies between 408 and 422  $m\mu$ , depending on the alkalinity of the solution.

The principle of our method is as follows. The sample is extracted with an organic solvent, and three aliquots of equal size are each evaporated to dryness under reduced pressure. One residue is hydrolysed with alkali. Benzene is added to another before the hydrolysis with alkali and both the reaction products are extracted with benzene - acetone mixture (1 + 4 by volume). The third residue is dissolved in 94 per cent. ethanol. The three solutions thus obtained are designated A, B and C.

The optical densities of solutions A and B are measured at 420  $m\mu$  against a blank solution identical with the test solution except that the sample has been omitted. The optical density of solution C is measured at 280  $m\mu$  against 94 per cent. ethanol.

In the calculation, the following designations are used—

A = the solution obtained after hydrolysis with alkali,

B = the solution obtained after treatment with benzene and hydrolysis with alkali,

C = the unhydrolysed ethanolic solution,

p = parathion,

- $N$  = *p*-nitrophenol,  
 $x$  = extraneous absorbing materials,  
 $\epsilon$  = molar extinction coefficient, and  
 $c$  = molar concentration.

It is assumed that the initial sample contains parathion, *p*-nitrophenol and extraneous materials that also absorb in the same regions.

According to Beer's law, we have the following equations—

$$\text{At wavelength } 420 \text{ m}\mu, E_A = {}_A E_P + E_N + {}_A E_x \quad \dots \dots \dots (1)$$

(in which  ${}_A E_P$  = the optical-density contribution of parathion in solution *A*),

$$\text{and } E_B = {}_B E_P + E_N + {}_B E_x \quad \dots \dots \dots (2)$$

$$\text{At wavelength } 280 \text{ m}\mu, E_C = E_P + E_N + E_x \quad \dots \dots \dots (3)$$

As no hydrolysis occurs when parathion is heated with alkali in the presence of benzene, and as parathion shows no absorption-at 420 m $\mu$ , then—

$${}_A E_P = {}_B E_P = 0.$$

Provided that the background absorption at 420 m $\mu$  caused by extraneous materials amounts to the same value in both solution *A* and solution *B*, then—

$${}_A E_x = {}_B E_x.$$

Subtraction of equation (2) from equation (1) gives—

$$E_A - E_B = {}_A E_{P \rightarrow N^0} \quad \dots \dots \dots (4)$$

As 1 mole of *p*-nitrophenol is formed from 1 mole of parathion, then according to Beer's law—

$$c_P = \frac{E_A - E_B}{\epsilon_N} \quad (\text{at wavelength } 420 \text{ m}\mu). \quad \dots \dots \dots (5)$$

From equations (1), (2) and (5), we can obtain the amount of *p*-nitrophenol formed on hydrolysis. This gives the true amount of *p*-nitrophenol, as the interfering absorbance due to extraneous materials is eliminated. On the other hand, if *p*-nitrophenol is the only substance present that absorbs at 420 m $\mu$ , its concentration before hydrolysis is given by the equation—

$$c_N = \frac{E_B}{\epsilon_N} \quad \dots \dots \dots (6)$$

The concentrations of both parathion and *p*-nitrophenol are thus found and, as the molar extinction coefficients of both substances are known, the optical-density values at 280 m $\mu$  can be calculated. If the sum of these calculated values is equal to the optical density of the unhydrolysed solution *C*, then parathion and *p*-nitrophenol only are present in the sample, and their identification is confirmed both qualitatively and quantitatively. Even in the presence of extraneous absorbing materials, the amount of *p*-nitrophenol formed on hydrolysis can be reliably ascertained.

## EXPERIMENTAL

### APPARATUS—

All spectrophotometric measurements were made with a Beckman DU spectrophotometer with use of 1-cm silica and Corex cells. Hydrolysis of the parathion was effected in a special separating funnel constructed for this purpose and shown in Fig. 2. The extraction of the sample, the subsequent evaporation of the extract to dryness under reduced pressure, the hydrolysis in a closed system and the extraction of the hydrolysed product were performed in this vessel.

### REAGENTS—

*Parathion*—This was further purified by dissolution in benzene and washing the benzene solution with dilute alkali, acid and water. The residue after evaporation of the benzene was dried in a vacuum-desiccator; it had  $d_{40}^{20^\circ\text{C}} = 1.2626$  and  $n_D^{20^\circ\text{C}} = 1.5369$ . The molar extinction coefficient of parathion in 94 per cent. ethanol measured at 280 m $\mu$  is 9426, which, for a concentration of 1  $\mu\text{g}$  per ml, is 0.032.

*p*-Nitrophenol—The Merck product was used. After recrystallisation, the melting-point was 112° C. The molar extinction coefficient in 94 per cent. ethanol measured at 280  $m\mu$  is 4210, which, for a concentration of 1  $\mu\text{g}$  per ml, is 0.030.

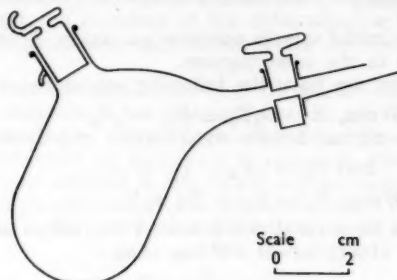


Fig. 2. Reaction vessel for the hydrolysis of parathion

All other reagents used were of recognised analytical grade.

Pure parathion was kindly supplied by the Institut für Gerichtliche Medizin an der Medizinischen Akademie Düsseldorf.

#### PRELIMINARY EXPERIMENTS—

Preliminary experiments for the spectrophotometric determination of *p*-nitrophenol in alkaline benzene - acetone solution were performed, and the hydrolysis of parathion in alkaline solution was investigated both in the presence and absence of benzene.

*The spectrophotometric determination of p-nitrophenol in alkaline benzene - acetone solution (1 + 4 by volume)*—To study the extraction of *p*-nitrophenol from a quantitative standpoint, the following experiments were performed—

- (i) *p*-Nitrophenol was dissolved in 5 or 10 ml of alkaline benzene - acetone solution. This was prepared by saturating the (1 + 4) mixture of benzene and acetone with 3.5 *N* potassium hydroxide.
- (ii) *p*-Nitrophenol was dissolved in 2 ml of 3.5 *N* potassium hydroxide and extracted from this solution with 10, 20 or three 10-ml portions of benzene - acetone mixture.

The solutions were diluted with alkaline benzene - acetone solution to a suitable volume, clarified with acetone in the volumetric ratio 4 to 1, and the optical densities were measured at 420  $m\mu$ . The results are shown in Table I.

TABLE I

#### EXTRACTION OF *p*-NITROPHENOL FROM POTASSIUM HYDROXIDE SOLUTION WITH BENZENE - ACETONE SOLUTION (1 + 4)

Weight of <i>p</i> -nitrophenol in 3.5 <i>N</i> potassium hydroxide solution, $\mu\text{g}$	Concentration of <i>p</i> -nitrophenol in final solution, $\mu\text{g}$ per ml	Optical density at 420 $m\mu$		Volume of benzene - acetone (1 + 4) used for extraction in experiment (ii), ml	Extinction coefficient for 1 $\mu\text{g}$ of <i>p</i> -nitrophenol per ml
		Experiment (i)	Experiment (ii)		
8	0.64	—	0.106	10	0.166
20	1.60	0.265	—	—	0.166
20	3.20	0.536	—	—	0.168
80	6.40	—	1.057	10	0.165
80	3.20	—	0.530	20	0.166
80	1.28	—	0.212	3 × 10	0.166
100	8.00	—	1.340	10	0.168
200	6.40	—	1.053*	10	0.165
400	6.40	—	1.040*	10	0.163
400	6.40	—	1.064	20	0.166
400	6.40	—	1.066	3 × 10	0.167

\* The alkali layer was yellowish.

The results in Table I show that 100  $\mu\text{g}$  of *p*-nitrophenol in 2 ml of 3.5 *N* potassium hydroxide are extracted quantitatively with 10 ml of benzene - acetone solution and amounts as high as 400  $\mu\text{g}$  can be extracted quantitatively with 20 ml of benzene - acetone. Further, it can be seen that the absorption of *p*-nitrophenol in alkaline benzene - acetone solution obeys Beer's law over the concentration range of 0.64 to 8.0  $\mu\text{g}$  per ml at 420  $m\mu$ .

*Hydrolysis of parathion*—Ketelaar<sup>19</sup> states that the hydrolysis of parathion with alkali is a bimolecular reaction; the half-time at 15° C with *N* alkali is 32 minutes. Biggs<sup>1</sup> reports that, when parathion is heated with ethanolic potassium hydroxide for 3 hours in sealed ampoules, the yield of *p*-nitrophenol is 87 per cent. In our work the hydrolysis was carried out by heating parathion with 3.5 *N* potassium hydroxide at 100° C in the reaction vessel shown in Fig. 2.

To determine the percentage hydrolysis, different amounts of parathion were hydrolysed and the *p*-nitrophenol formed was determined as described previously. The results are given in Table II.

TABLE II  
HYDROLYSIS OF PARATHION IN 3.5 *N* POTASSIUM HYDROXIDE  
AT 100° C FOR 2 HOURS

Amount of parathion present, $\mu\text{g}$	Weight of <i>p</i> -nitrophenol found, $\mu\text{g}$	Calculated amount of parathion, $\mu\text{g}$	Hydrolysis, %
40	18.2	38.1	95.3
41	18.0	37.8	94.9
60	27.4	57.4	95.6
80	35.2	73.7	92.1
82	36.3	76.0	92.7
82	37.5	78.5	95.7
120	52.8	110.6	92.2
123	55.2	115.6	94.0
160	71.4	149.5	93.4

It can be seen that the hydrolysis varied between 92.1 and 95.7 per cent., the mean value being 93.7 per cent.

*Hydrolysis of parathion in the presence of benzene*—It was observed that benzene prevents the hydrolysis of parathion by alkali. Experiments were therefore made in which parathion was allowed to stand in benzene and was then boiled with strong alkali. In other experiments, parathion was allowed to stand in alkaline acetone solution both with and without the addition of benzene.

Different amounts of parathion in 2 ml of benzene were treated with alkali. Some of these benzene solutions were shaken with 2 ml of 3.5 *N* potassium hydroxide and the mixtures were kept at room temperature for 24 hours, with intermittent shaking. The other solutions were boiled under reflux with 2 ml of 3.5 *N* potassium hydroxide for 2 hours. The phases were separated and the benzene layer was washed with dilute acid and with water. One millilitre of the washed benzene solution was removed by pipette and evaporated to dryness under reduced pressure at 50° C. The residue after evaporation was dissolved in 94 per cent. ethanol and the optical density of the solution was measured at 280  $m\mu$ . The results are shown in Table III.

TABLE III  
HYDROLYSIS OF PARATHION IN BENZENE WITH 3.5 *N* POTASSIUM HYDROXIDE

Initial concentration of parathion, $\mu\text{g}$ per 2 ml	Amount recovered after 24 hours at room temperature, $\mu\text{g}$ per 2 ml	Amount recovered after 2 hours at 100° C, $\mu\text{g}$ per 2 ml
80	79.1	78.4
120	118.6	119.3
160	159.7	160.3
2000	—	2001.1

From Table III it can be seen that no hydrolysis occurs when benzene is used as the solvent. In benzene, parathion can be heated with strong alkali, treated with dilute acid and with water, and freed from the organic solvent without any loss.

In other experiments, different amounts of parathion were dissolved in 8 ml of acetone, and in 10 ml of the (1 + 4) benzene - acetone mixture. The solutions were shaken with 2 ml of 3.5 *N* potassium hydroxide for 1 minute and set aside at room temperature for different lengths of time. The reaction times were 1, 3 and 24 hours. Two millilitres of benzene were then added to the solutions containing acetone as the solvent, and the solutions were shaken again. After separation of the phases, the benzene - acetone layer was prepared for spectrophotometric measurement as described under "Procedure." The results are shown in Table IV.

TABLE IV  
HYDROLYSIS OF PARATHION IN ALKALINE SOLUTIONS OF ACETONE  
AND BENZENE - ACETONE (1 + 4)

Concentration of parathion, $\mu\text{g}$ per ml	Reaction time, hours	With acetone as solvent—		With benzene - acetone solution (1 + 4) as solvent—	
		optical density at 420 $m\mu$	amount of <i>p</i> -nitrophenol formed, $\mu\text{g}$	optical density at 420 $m\mu$	amount of <i>p</i> -nitrophenol formed, $\mu\text{g}$
40	1	0.006	0.0	0.002	0.0
	3	0.022	1.7	0.007	0.0
	24	0.117	8.8	0.051	3.8
80	1	0.016	0.0	0.004	0.0
	3	0.047	3.5	0.007	0.0
	24	0.221	16.7	0.109	8.2

The results in Table IV show that, in alkaline acetone solution, parathion is appreciably hydrolysed during the first 3 hours, and more than 40 per cent. is hydrolysed in 24 hours. In the presence of benzene, however, hydrolysis is retarded. No absorption due to *p*-nitrophenol can be detected after 3 hours and only about 20 per cent. of parathion is hydrolysed in 24 hours.

The optical density of parathion together with the optical density due to extraneous materials can therefore be measured without interference from the hydrolysis, provided that the reaction time does not exceed 3 hours.

#### METHOD

##### PROCEDURE—

*Hydrolysis of parathion*—Parathion is dissolved in an organic solvent and an aliquot containing from 20 to 200  $\mu\text{g}$  is transferred by pipette to the reaction vessel. The solution is evaporated to dryness under reduced pressure at 50° C. Two millilitres of 3.5 *N* potassium hydroxide are added to the residue, the stopper is fastened with a rubber band and the vessel is placed in a boiling-water bath. After 30 seconds, the stopcock is closed and heating is continued for 2 hours. After cooling, 5 to 20 ml ( $V_1$ ) of benzene - acetone solution (1 + 4) are added, the mixture is shaken for 1 minute and then set aside for 10 minutes, after which the alkali layer is removed. Four millilitres of the benzene - acetone layer are removed by pipette and mixed with 1 ml of pure acetone. This solution is used for the spectrophotometric determination. The optical density of this solution, which is designated solution A, remains unchanged for at least 24 hours.

*Determination of p-nitrophenol and the background absorption*—An aliquot of equal size to that used for the hydrolysis is placed by pipette in the reaction vessel and evaporated to dryness. From 1 to 4 ml of benzene are added to the residue, and then 2 ml of 3.5 *N* potassium hydroxide. A reflux condenser is attached to the vessel and the solution is heated under reflux in a water bath for 2 hours. After it has cooled, the solution is shaken with 4 to 16 ml of acetone, and the layers are separated. Four millilitres of the benzene - acetone layer are removed by pipette and diluted with 1 ml of acetone. This solution is used for the spectrophotometric determination. The optical density of this solution, which is designated solution B, remains unchanged for 3 hours.

*Preparation of the blank solution*—Ten millilitres of benzene - acetone solution (1 + 4) are shaken with 2 ml of 3.5 *N* potassium hydroxide. The layers are separated and 4 ml of the benzene - acetone layer are removed by pipette and diluted with 1 ml of acetone. This is the blank solution. Its optical density remains unchanged for at least 24 hours.

**Preparation of the control solution**—An aliquot of equal size to that used for the hydrolysis is evaporated to dryness. The residue is dissolved in 5 to 20 ml ( $V_2$ ) of 94 per cent. ethanol. This is solution C.

**Measurement of optical density**—The optical densities of solutions A and B are measured against the blank solution at 420  $m\mu$ . This gives the values of  $E_A$  and  $E_B$  in equations (1) and (2), p. 285. The optical density of solution C is measured at 280  $m\mu$  against 94 per cent. ethanol. This gives the value for  $E_C$  in equation (3).

**Paper-chromatographic detection of *p*-nitrophenol**—The hydrolysed and unhydrolysed solutions are chromatographed. By using the ascending-solvent technique with a (1 + 1) mixture of isobutyl and isoamyl alcohols saturated with ammonia as solvent; the  $R_F$  value for *p*-nitrophenol is 0.48. The chromatograms are allowed to develop at 23° C for 18 hours. The spots are detected by spraying with ammonia or alkali.

#### CALCULATIONS—

To calculate the results, the constants for a concentration of 1  $\mu\text{g}$  per ml are as follows—

For *p*-nitrophenol in solutions A and B at 420  $m\mu$ ,  $\epsilon_N = 0.166$ .

For *p*-nitrophenol in ethanol at 280  $m\mu$ ,  $\epsilon_N = 0.0303$ .

For parathion in ethanol at 280  $m\mu$ ,  $\epsilon_P = 0.0324$ .

The percentage hydrolysis is 93.7, and the molecular weights of parathion and *p*-nitrophenol are 291.3 and 139.1, respectively. Hence the concentration of parathion is given by—

$$c_P = 2.23 \times \text{concentration of } p\text{-nitrophenol in solution A.}$$

If  $V_1$  is the volume of benzene-acetone solution, and  $V_2$  the volume of ethanol used, then, by applying equation (5), the amount of parathion per aliquot is given by—

$$16.8 \times V_1 \times (E_A - E_B) \mu\text{g.}$$

The corresponding optical density measured at 280  $m\mu$  is—

$$E_P = 0.545 \times \frac{V_1}{V_2} \times (E_A - E_B).$$

From equation (6)—

$$\text{Weight of } p\text{-nitrophenol per aliquot} = 7.54 \times V_1 \times E_B \mu\text{g.}$$

The corresponding optical density measured at 280  $m\mu$  is given by—

$$E_N = 0.227 \times \frac{V_1}{V_2} \times E_B.$$

If the sum of the calculated values for  $E_P$  and  $E_N$  is equal to  $E_C$  (all measured at 280  $m\mu$ ), the amounts of both parathion and *p*-nitrophenol are confirmed. If this sum is smaller than  $E_C$ , the amount of *p*-nitrophenol formed on hydrolysis can be determined.

#### RESULTS

Prepared mixtures of parathion and *p*-nitrophenol and some commercial preparations were analysed. The results of four such analyses calculated in micrograms per millilitre are given below. In each analysis both  $V_1$  and  $V_2$  were 10 ml.

(i) A solution containing 80  $\mu\text{g}$  of parathion and 21.9  $\mu\text{g}$  of *p*-nitrophenol in 1 ml of benzene was prepared. The presence of *p*-nitrophenol was detected, both before and after hydrolysis, by paper-chromatographic techniques.

$E_A$  was 0.768 and  $E_B$  was 0.286, therefore  $E_A - E_B$  was 0.482. The amount of *p*-nitrophenol found was 21.6  $\mu\text{g}$ , for which, at 280  $m\mu$ ,  $E_N = 0.065$ . The amount of parathion found was 80.9  $\mu\text{g}$ , for which, at 280  $m\mu$ ,  $E_P = 0.263$ .

$$E_P + E_N = 0.328.$$

It was found that, at 280  $m\mu$ ,  $E_C = 0.336$ .

From these results it can be concluded that the sample contains 80.9  $\mu\text{g}$  of parathion and 21.6  $\mu\text{g}$  of *p*-nitrophenol.

(ii) A commercial powder contains about 20 per cent. of parathion, according to specification. An extract containing 200  $\mu\text{g}$  of the sample in 1 ml of benzene was prepared. The paper-chromatographic study showed that, before hydrolysis, no *p*-nitrophenol was present, but after hydrolysis a positive result was obtained.

$E_A$  was 0.284 and  $E_B$  was 0.001, therefore  $E_A - E_B$  was 0.283. No *p*-nitrophenol was found, and the amount of parathion found was 47.5  $\mu$ g, for which, at 280  $m\mu$ ,  $E_P = 0.154$ .

$$E_P + E_N = 0.154 + 0 = 0.154.$$

It was found that, at 280  $m\mu$ ,  $E_C = 0.157$ .

From these results it can be concluded that the sample contains about 23.7 per cent. of parathion.

(iii) A commercial fluid contains about 35 per cent. of parathion, according to specification. An extract containing 133.9  $\mu$ g of the sample in 1 ml of benzene was prepared. The paper-chromatographic study showed the presence of *p*-nitrophenol both before and after hydrolysis.

$E_A$  was 0.263 and  $E_B$  was 0.036, therefore  $E_A - E_B$  was 0.227. The amount of *p*-nitrophenol found was 2.7  $\mu$ g, for which, at 280  $m\mu$ ,  $E_N = 0.008$ , and the amount of parathion found was 38.2  $\mu$ g, for which  $E_P = 0.124$ .

$$E_P + E_N = 0.132.$$

It was found that  $E_C = 0.161$ .

From these results it can be concluded that the sample contains about 28.5 per cent. of parathion, not more than 2.0 per cent. of *p*-nitrophenol and extraneous absorbing materials.

(iv) A commercial fluid contains 33.5 per cent. of parathion, according to specification. An extract containing 126.9  $\mu$ g of the sample in 1 ml of benzene was prepared. The paper-chromatographic study showed the presence of *p*-nitrophenol both before and after hydrolysis.

$E_A$  was 0.346 and  $E_B$  was 0.092, therefore  $E_A - E_B$  was 0.254. The amount of *p*-nitrophenol found was 6.9  $\mu$ g, for which, at 280  $m\mu$ ,  $E_N = 0.021$ . The amount of parathion found was 42.7  $\mu$ g, for which  $E_P = 0.138$ .

$$E_P + E_N = 0.159.$$

It was found that  $E_C = 0.235$ .

From these results it can be concluded that the sample contains about 33.6 per cent. of parathion, not more than 5.4 per cent. of *p*-nitrophenol and extraneous absorbing materials.

#### CONCLUSIONS

By using the proposed method the *p*-nitrophenol formed on hydrolysis of parathion can be determined. The background absorption does not interfere with the determination, as it can be measured separately. The method is applicable to the determination of parathion in commercial preparations.

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# The Determination of Ethanol and Acetaldehyde in Plant Tissue by Low-temperature Diffusion

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A method for the determination of ethanol and acetaldehyde is proposed, based on the transfer of volatile substances from frozen tissue to aqueous sulphuric acid by evaporation and diffusion. The determination is easy to carry out, but the diffusion requires a long time. The material is maintained at a low temperature and the method, therefore, is theoretically preferable to a distillation method. The amount of acetaldehyde volatilised from peas is shown to be much greater when it is distilled in steam than when it is volatilised at a low temperature.

ETHANOL and acetaldehyde have been separated from plant tissue by steam-distillation.<sup>1</sup> When the total amount of acetaldehyde and ethanol is small, either by reason of a very low concentration or because of the small size of sample available, the loss during normal steam-distillation is serious, with the result that a procedure has to be adopted in which any uncondensed vapour of ethanol or acetaldehyde is trapped. Besides this practical difficulty, all distillation methods have the disadvantage that the tissue is heated for relatively long periods, during which volatile interfering compounds may be produced (perhaps even ethanol or acetaldehyde). It was found, for instance, that repeated distillations of the same sample of peas in water gave a slow but continuing production of volatile substances, see Table IV, p. 295, and an extract of potatoes under acid conditions gave rise to large amounts of volatile material.<sup>2</sup>

Separation of ethanol from blood or urine by volatilisation at about room temperature has been proposed by Widmark,<sup>3</sup> Winnick<sup>4</sup> and Cavett,<sup>5</sup> but, if applied to plant material, it is likely to be open to the same objections as the distillation method and the preparation of sub-samples of vegetable tissue, suitable for the method, presents great difficulty.

In view of these difficulties, the theoretically much sounder alternative of volatilising the ethanol from the material in the frozen state was considered. In practice, frozen peas were held over sulphuric acid in a sealed container at a low temperature. Water and other volatile substances evaporated from the frozen tissue and diffused to the sulphuric acid with about the same time of half-transfer. At a low temperature, *i.e.*,  $-20^{\circ}\text{C}$ , there should be little risk of production or destruction in the material of either ethanol or acetaldehyde and both should be stable in the sulphuric acid. Unfortunately, at  $-20^{\circ}\text{C}$  the time required for transfer of ethanol to the sulphuric acid was unreasonably long and a temperature of  $-12^{\circ}\text{C}$  was used instead. Even at this temperature 70 to 100 days were required for complete transfer of the ethanol from 20 to 40 g of whole peas. Movement of volatile substances from the peas was relatively rapid at first, but, as the outer layers dried, an additional resistance to diffusion arose and the rate slowed down progressively. The water content of much of the pea was low for most of this 100-day period, so that side reactions were presumably considerably reduced compared with frozen wet material stored at  $-12^{\circ}\text{C}$ .

## EXPERIMENTAL

### DETERMINATION OF ETHANOL AND ACETALDEHYDE—

The reducing value of the absorbed volatile substances was determined iodimetrically by the amount of chromic acid required to oxidise them in aqueous 50 per cent. sulphuric acid at  $100^{\circ}\text{C}$ , as described by Kozelka and Hine.<sup>6</sup> The reducing value equivalent to the acetaldehyde is subtracted and the residual reducing value has been treated as ethanol.

Acetaldehyde was determined by a modification of the colorimetric method proposed by Barker and Summerson,<sup>7</sup> in which acetaldehyde in diluted sulphuric acid (6 + 1 v/v) is treated with *p*-hydroxydiphenyl. The changes introduced are (a) the mixture of acetaldehyde and copper sulphate with diluted sulphuric acid (6 + 1 v/v) is cooled in iced water, (b) double the amount of *p*-hydroxydiphenyl reagent is used, and (c) the reaction is allowed

to proceed at 20° C for 30 minutes. Batches of sulphuric acid tested were found to be liable to have a low and variable negative blank value for acetaldehyde and, to overcome this, acetaldehyde was added to all the acid used until a small positive blank value was obtained.

#### SEPARATION OF VOLATILE SUBSTANCES BY DISTILLATION—

A distillation method was designed, in which peas in water, *i.e.*, at their natural pH of about 6.5, were distilled at 100° C for 30 minutes. Loss of acetaldehyde and of ethanol from the collecting end was prevented by the use of a scrubber of aqueous 50 per cent. sulphuric acid followed by one of diluted sulphuric acid (6 + 1 v/v). Distillation of 40 mg of ethanol from pure solutions gave a mean recovery of 99.6 per cent. (range of 7 tests, 99.2 to 100.0 per cent.) and of 200  $\mu$ g of acetaldehyde gave a mean recovery of 98.6 per cent. (range of 8 tests, 97.7 to 102.6 per cent.). Replicate samples of pea powder also gave good agreement.

#### SEPARATION OF VOLATILE SUBSTANCES BY DIFFUSION—

The chemical methods used in this work require the ethanol to be dissolved in aqueous 50 per cent. sulphuric acid and the acetaldehyde in sulphuric acid diluted exactly (6 + 1 v/v). To obtain the maximum concentration of the ethanol for subsequent determination, it should be volatilised into the least volume of sulphuric acid that will give a concentration of just above 50 per cent. at the end of the diffusion. Ethanol is quantitatively absorbed by acid of this or higher concentration.

The quantitative absorption of acetaldehyde is difficult for two reasons. First, during the transfer of acetaldehyde to sulphuric acid of high concentration there is always some destruction of the acetaldehyde, and there is a further continuing slow loss on standing. This loss was greatest in pure sulphuric acid and less when the acid was diluted with water; with aqueous 70 per cent. sulphuric acid it was small and with 50 per cent. could not be detected. Secondly, there is a significant concentration of free acetaldehyde in 50 per cent. sulphuric acid, which decreases as the concentration of acid is raised and in 85 per cent. sulphuric acid is insignificant. This free acetaldehyde sets up a vapour pressure in the gas phase and, in consequence, absorption by 50 per cent. sulphuric acid is incomplete. As a compromise between these opposing requirements, the highest concentration of sulphuric acid used was 66 per cent. and this fell to about 50 per cent. by uptake of water during the diffusion. In this way destruction of acetaldehyde was avoided, but absorption was incomplete. These concentrations resulted in the use of a large volume of sulphuric acid with consequent dilution of the ethanol. If ethanol alone is being determined, it is best to use sufficient pure sulphuric acid to end the diffusion with a concentration of 50 per cent.

Determinations are carried out in a crystallising dish that has a rim ground to make a good fit with a thick glass plate that serves as a lid. There is a small hole in the lid that is sealed with a glass slide. A sealing compound, such as Vaseline, that hardens at -12° C is put round the rim of the dish and the calculated amount of 66 per cent. v/v sulphuric acid is added by weighing. A small glass tripod supporting a wire tray to contain the peas is next put in and the whole is cooled to -12° C. Then, as rapidly as possible, the dish is brought out of the cold chamber, the peas, at -20° C, are transferred to the tray, the lid, still at room temperature (to soften the sealing compound), is put on and weighted down and the whole is returned to -12° C. The hard sealing compound and the weight are to prevent leaks arising from changes in barometric pressure during the diffusion. For peas, the transfer of acetaldehyde and ethanol is sensibly complete within 70 to 100 days, but other material might require a shorter time. At the end of this period the dish is warmed to room temperature, the peas and tripod are rapidly removed, the lid is replaced and the acid is made to exactly 50 per cent. v/v by the addition of water through the hole in the lid until the correct weight is attained. After mixing, an aliquot of the acid is withdrawn through the hole in the lid and added to sufficient pure sulphuric acid to make the concentration exactly (6 + 1). Acetaldehyde is determined on this solution and ethanol on a sub-sample of the main bulk of the sulphuric acid. Loss of acetaldehyde from the diffusion chamber, which is relatively rapid, must be guarded against during these manipulations.

As a check on the completeness of transfer, the peas may be replaced at -12° C over fresh acid. This is best done in a smaller dish, as only a small volume of 50 per cent. sulphuric acid is required since the peas are dry.

## RESULTS AND DISCUSSION

Results of two experiments in which dilute aqueous solutions of acetaldehyde and of ethanol were determined after transfer to sulphuric acid either by direct dilution (controls) or by diffusion are given in Table I. The accuracy of the determination of ethanol by diffusion is clearly high and similar to that with the distillation apparatus. A comparison of the two methods was made on 5-g portions of a bulk sample of ground frozen peas. The results of replicate determinations by steam-distillation for 30 minutes were 8.9, 8.9, 9.2 and 9.4 mg and by diffusion at  $-12^{\circ}\text{C}$  for 30 days were 8.6, 8.6, 9.15 and 9.4 mg, which shows that both methods gave similar values for the ethanol content of peas.

TABLE I

## RECOVERY OF PURE ETHANOL AND ACETALDEHYDE BY DIFFUSION

Diffusion was carried out for 5 days at  $20^{\circ}\text{C}$ 

Ethanol found in controls by direct dilution, mg	Mean, mg	Ethanol found by diffusion,* mg	Mean, mg	Recovery, %	Acetaldehyde found in controls by direct dilution, $\mu\text{g}$	Mean, $\mu\text{g}$	Acetaldehyde found by diffusion,† $\mu\text{g}$	Mean, $\mu\text{g}$	Recovery, %
39.3	39.33	39.4	39.4	100.2	212	215	200	204	94.9
39.3		39.4			218		205		
39.4		39.4			215		208		

\* Determined by volatilising 5 ml of water containing 40 mg of ethanol into 15 ml of 66 per cent. sulphuric acid. Each value is the mean of three determinations.

† Determined by volatilising 5 ml of water containing about 200  $\mu\text{g}$  of acetaldehyde into 95 ml of 52.6 per cent. sulphuric acid. Each value is the mean of two determinations.

The recovery of acetaldehyde from pure solutions, about 95 per cent. (see Table I), is not as good as with the distillation apparatus because of the incomplete absorption of acetaldehyde by 50 per cent. sulphuric acid. At  $20^{\circ}\text{C}$  there is in the gas phase a concentration of about 0.5 per cent. of that in the sulphuric acid, and, since the gas volume is large compared with that of the acid, the loss due to this cause is appreciable. The diffusion vessel has first to be opened to remove the material, and then allowed to re-equilibrate, with a double loss of acetaldehyde (about 3 to 4 per cent. each time when the ratio of volume of acid to gas phase is about 1 to 7). The recovery by this method, therefore, is not complete, but the loss results from a known physical cause and its size can be reasonably accurately assessed, whereas in other methods unknown chemical factors may result in large apparent errors (see below).

TABLE II

TRANSFER OF ETHANOL AND ACETALDEHYDE FROM ABOUT 30 TO 40 g OF FROZEN WHOLE PEAS INTO ABOUT 100 ml OF 66 PER CENT. SULPHURIC ACID AT  $-12^{\circ}\text{C}$ 

Period, days	Ethanol found in experiment 1, mg per 100 g fresh weight	Ethanol found in experiment 2, mg per 100 g fresh weight	Acetaldehyde found in experiment 1, $\mu\text{g}$ per 100 g fresh weight	Acetaldehyde found in experiment 2, $\mu\text{g}$ per 100 g fresh weight
<b>9.7.52</b>				
0 to 30	42.9	251	1390	2240
30 to 50	9.2	23.2	510	590
50 to 70	3.1	2.1	330	60
70 to 97	1.2	1.6	30	10
<b>22.7.53</b>				
0 to 52	138	217	2560	1990
52 to 85	15.7	16.3	780	680
85 to 105	1.5	2.3	270	360
105 to 137	1.3	1.1	10	50
<b>21.7.52</b>				
0 to 50	166	211	1470	4020
50 to 73	0.5	0.2	20	30

The amounts of ethanol and acetaldehyde transferred in successive periods at  $-12^{\circ}\text{C}$  are shown for several experiments in Table II. No reason is known for the variation in rate of transfer of ethanol in different experiments—it might have been an expression of the

permeability of the testa of the peas or of the form of the ice crystals in the frozen pea, which would affect the porosity of the dry tissue. There was clearly only a very small continuing production of either volatile substance, but this, unfortunately, cannot be used as proof that there was no production in the earlier stages, since the material is wet in one case and dry in the other. In many of the experiments, as in the first two quoted, the proportion of the total acetaldehyde volatilised in the second period (sometimes in the third also) was higher than the corresponding proportion of ethanol, which suggests that there was some degree of binding of acetaldehyde to a non-volatile component of the system. However, it was always possible to continue diffusion until the transfer of acetaldehyde became negligibly small.

The rate of migration of volatile substances is obviously much influenced by the length of the diffusion path and therefore the distance from the peas to the acid surface should be as short as possible. The volume of acid required depends only on the volume of water to be transferred; therefore the size of the sample, and with it the crystallising dish and volume of acid, can be altered over a very wide range with no change in over-all accuracy. There seems to be no reason why it should not be done on a micro scale if required—the difficulty would be to get the sample of frozen material into the apparatus without loss of volatile substances, which, when the tissue is at  $-20^{\circ}\text{C}$ , may be present in relatively high concentration in the unfrozen phase of the tissue.

The acetaldehyde content found in similar samples of peas when determined by the distillation method in 1951 and 1955 was markedly higher than that found from 1952 to 1954 by the diffusion method (see Table III). The size of this difference between the two methods clearly depends on the condition of the pea, being least in mature and most in wilted old peas. Changes in acetaldehyde content, induced by experimental conditions, were similar in magnitude when determined by either method, which suggests that an excess production of acetaldehyde occurs during the distillation procedure that is dependent on the condition of the peas. Evidence of such production was sought by repeatedly distilling the same sample of peas (see Table IV).

TABLE III

ACETALDEHYDE CONTENT OF COMPARABLE RANGES OF SAMPLES OF PEAS IN DIFFERENT SEASONS

Steam-distillation was carried out for 30 minutes and diffusion was carried out at  $-12^{\circ}\text{C}$  for periods of between 50 and 106 days

Acetaldehyde found by steam-distillation in—					Acetaldehyde found by diffusion in—				
Season	mature peas, $\mu\text{g}$ per 100 g fresh weight	old peas, $\mu\text{g}$ per 100 g fresh weight	wilted mature peas, $\mu\text{g}$ per 100 g fresh weight	wilted old peas, $\mu\text{g}$ per 100 g fresh weight	Season	mature peas, $\mu\text{g}$ per 100 g fresh weight	old peas, $\mu\text{g}$ per 100 g fresh weight	wilted mature peas, $\mu\text{g}$ per 100 g fresh weight	wilted old peas, $\mu\text{g}$ per 100 g fresh weight
1951	630	410	1772	2400	1952	400	20	700	—
	520	550	1762	1450		410	60	660	—
	850	420	—	—		460	—	400	—
	520	—	—	—		480	—	—	—
	—	—	—	—		480	—	—	—
1955	1180	330	—	—	1953	—	100	460	90
	—	160	—	—		—	—	430	80
	—	520	—	—		—	—	380	110
	—	230	—	—	1954	420	—	390	110
Mean	740	370	1770	1900	Mean	440	60	490	100

In the sample of peas with a high content of ethanol (sample B) all but 3 per cent. of the ethanol was distilled over in the first 30 minutes, and a greater proportion of acetaldehyde, being more volatile, should have been removed by a similar period of distillation. In fact, successive distillations liberated large amounts of acetaldehyde, which must have been produced during the distillation. In the first distillate there should be all the free acetaldehyde together with some from the same source as that liberated in subsequent distillations. The amount of this "non-free" acetaldehyde is difficult to assess, but the results in Table IV suggest that it was probably not less than  $200\text{ }\mu\text{g}$  in the mature peas tested and  $150\text{ }\mu\text{g}$  in

the old peas. Such an excess of "non-free" acetaldehyde is, for mature peas, comparable with the mean difference between the results by diffusion and distillation (see Table III), but for old peas it is lower (this may be because the old peas used were very low in acetaldehyde). It is clear that the values for the acetaldehyde content of peas obtained by the distillation method have a large and variable error and therefore the lower values obtained by diffusion become more probable.

TABLE IV

ETHANOL AND ACETALDEHYDE GIVEN OFF DURING SUCCESSIVE STEAM-DISTILLATIONS FOR 30 MINUTES OF THE SAME SAMPLE OF PEAS

Distillation No.	Acetaldehyde driven off from mature peas, $\mu\text{g}$ per 100 g fresh weight	Acetaldehyde driven off from old peas, $\mu\text{g}$ per 100 g fresh weight	Distillation No.	Ethanol driven off from sample A (aerobic), mg per 100 g fresh weight	Ethanol driven off from sample B (anaerobic), mg per 100 g fresh weight
1	1180	229	1	37.2	55.3
2	145	98	2	13.9	17.2
3	106	61	3	8.1	6.9
4	76	47	4	—	3.4
5	66	54			
6*	246	261			

\* Sample heated under reflux at  $100^\circ\text{C}$  for 2 hours and then steam-distilled for 30 minutes.

The compound broken down during the distillation is not likely to have been a normal acetaldehyde addition compound, as such a compound would probably have a higher vapour pressure of acetaldehyde than occurred in tests in the diffusion apparatus—by the final period of diffusion there was less than 1 to 2  $\mu\text{g}$  of free acetaldehyde in the whole system with a volume of 1100 ml of air and 100 ml of sulphuric acid.

The two methods gave values for the ethanol content of peas that agreed when portions of a bulk sample were compared or when similar samples were tested by a different method in successive seasons. Repeated distillation of the same sample of peas showed that there was a small and decreasing production of volatile reducing material, which seems to be independent of the total ethanol content of the peas, and as such is only serious at low ethanol concentrations.

In complex systems, such as living tissue, it is seldom possible to determine the content of reactants in the living state. Results are nearly always based on the content found in dead material and this may differ from that in the living material, depending both on the method of killing and the method of extraction, since even after death some of the wide range of compounds present may interact, especially if heated. Differences between tissue killed at a high and a low temperature, for instance, have been shown to exist by Isherwood and Niavis<sup>8</sup> in the determination of keto acids in plant material. In the work described in this paper, the excess of acetaldehyde appears to arise as a result of heat treatment subsequent to the death of the tissue, i.e., it is probably non-enzymic in origin.

On general grounds, a method of killing and extraction carried out at a low temperature, when reaction rates are slow, is to be preferred to one that involves heating, and such a method has a greater intrinsic probability of giving an estimate of the compounds present during life.

The work described in this paper was carried out as part of the programme of the Food Investigation Organisation of the Department of Scientific and Industrial Research. The experimental part of the investigation was carried out by Mr. J. R. Howe.

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## The Rapid Determination of Carbon and Hydrogen in Highly Volatile Combustible Organic Liquids

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A method is described for the rapid determination of carbon and hydrogen in organic liquids of low boiling-point, such as benzene, toluene, gasoline and other petroleum distillates. The method is also applicable to solutions in solvents of low boiling-point and to mixtures of organic liquids or solids of low and high boiling-points. As such samples are too volatile to be weighed in open containers, a special weighing tube has been designed that avoids the difficulty of using a sealed weighing capillary. Moreover, the evaporation of the sample is carried out in a current of nitrogen; by accurate control of the rate of flow the evaporation can also be controlled. After the volatile portion of the sample has been carried over and burnt, the non-volatile portion, if any, is burnt at an elevated temperature in a current of oxygen passed through the sample tube. The test takes about 45 minutes and gives accurate results. Replicate determinations generally lie within  $\pm 0.14$  per cent. for carbon and  $\pm 0.07$  per cent. for hydrogen.

THE determination of carbon and hydrogen in highly volatile organic liquids is important in the analysis of petroleum, coal, tar hydrogenation products and so on. One of the earlier methods is that of Liebig. In this method the sample is taken in a bulb, the open end of which is drawn out into a capillary that is sealed before it is weighed. The sealed tube is placed in a boat and is introduced into a combustion tube after the sealed end has been broken. The sample is burnt in a current of oxygen as usual. There are several drawbacks to this method. If the boiling-point of the substance is very low, there is the danger of an explosion caused by rapid evaporation and the resulting back pressure. Also, specks of carbon may remain, which cannot be burnt off without smashing the bulb.

Subsequent workers have endeavoured to eliminate these disadvantages. Clarke<sup>1</sup> has suggested a method in which one end of the combustion tube is drawn out and a ground-glass socket fused to it. The liquid to be analysed is weighed in a U-tube, to one side-tube of which is fused the corresponding ground-glass cone. The stopcock in each arm is greased with soft paraffin wax. The sample is weighed in the U-tube and carried into the combustion tube by the oxygen stream. Combustion is reported to take place smoothly.

The main drawback to this method is that, if the sample contains any solid in solution, a part of the sample remains in the U-tube and causes low results. Another point worthy of mention is that, if the sample is highly volatile, some of the air inside the U-tube may be expelled by the vapour from the liquid before the stopcocks are closed. This would give high results. When highly volatile liquids are used the risk of explosion is also present.

Many other workers, *e.g.*, Reid,<sup>2</sup> Brunn and Faulconer<sup>3</sup> and Avery and Hayman,<sup>4</sup> have suggested similar methods, but none is entirely free from the defects previously mentioned. Levin and Uhrig,<sup>5</sup> Bailly,<sup>6</sup> Aluise<sup>7</sup> and Sevag<sup>8</sup> have suggested improvements, but in all these methods the difficulties of weighing the sample and the danger of explosion are not completely overcome.

The essential features of the proposed method are—

- (i) easy and accurate weighing of the sample;
- (ii) the danger of explosion is avoided;
- (iii) smooth combustion;
- (iv) accurate analysis of highly volatile pure organic liquids or their mixtures, or solutions of solids in such liquids;
- (v) simplicity of apparatus and ease of manipulation.

## METHOD

## APPARATUS—

The weighing tube consists of a 1-mm Pyrex-glass capillary of external diameter 6 mm. Three bulbs are blown in the capillary, as shown in Fig. 1. The largest bulb, C, is 35 mm long and has an external diameter of 13 mm, and the two smaller bulbs, A and B, each have an external diameter of 9 mm. The bulb A, in which the sample is weighed, holds 0.15 to 0.2 g.

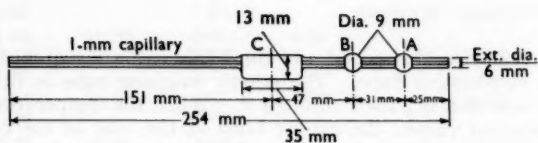


Fig. 1. Weighing tube

The purification trains consist of a flow meter to measure the rate of flow of gas, a sulphuric acid bubbler, an empty bubbler to trap the acid spray, a U-tube packed with Carbo-sorb soda asbestos and a U-tube packed with anhydron to remove carbon dioxide and moisture, respectively, from the gas before it enters the combustion tube. Two purifying trains are used, one to purify oxygen and the other to purify nitrogen.

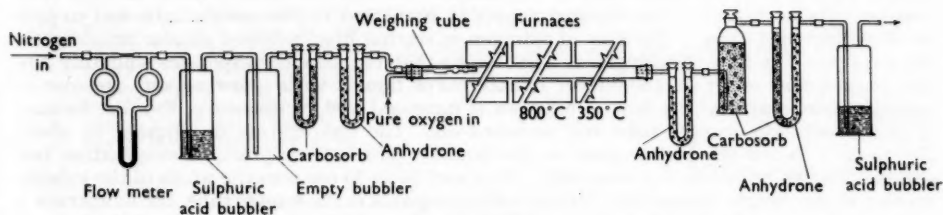


Fig. 2. Arrangement of apparatus with purifying and absorption trains

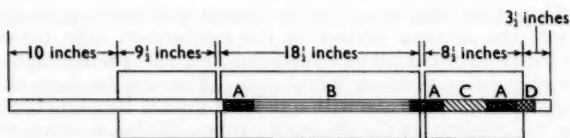


Fig. 3. Packing of the combustion tube: zones A, 1 to 2 inches of oxidised copper gauze; zone B, 16 inches of copper oxide; zone C, 5 inches of red lead; zone D, 3 inches of silver gauze

The absorption train consists of a U-tube packed with anhydron, a Midvale tube packed with Carbo-sorb soda asbestos, a guard U-tube packed with Carbo-sorb soda asbestos in one limb and anhydron in the other and a sulphuric acid bubbler to allow observation of the rate of flow of the exit gas.

A three-unit Liebig furnace is used for the combustion. The temperature of the first furnace can be raised from 30° to 600° C in 30 minutes, the second and longest furnace is maintained at 800° C and the third at 350° C. A silica combustion tube 50 inches long, the first 20 inches of which are transparent, is used.

The combustion tube is closed at the exit end by a rubber bung with a glass tube passing through it for connection to the absorption train and at the inlet end by a rubber bung with two holes. Through one hole a glass tube is fitted for connection to the oxygen purifying train and the weighing tube is fitted through the other, as shown in Fig. 2. This also serves as the nitrogen inlet to the combustion tube. The complete packing of the combustion tube is shown in Fig. 3. The red lead is prepared by making a paste of lead peroxide with water, drying it, cutting it into cubes and then heating it at  $400^{\circ}\text{C}$  for 4 to 5 hours in a muffle furnace.

#### PROCEDURE—

To start a determination the second and third furnaces are switched on and oxygen is passed through the combustion tube. The empty weighing tube is fitted in position as shown in Fig. 2 and nitrogen is passed through it. When the temperatures of the furnaces have risen to the required values, the rubber bung at the inlet of the combustion tube is taken out and the weighing tube is detached. The combustion tube is now closed with a rubber bung carrying a glass tube connected to the oxygen supply. The flushing of the apparatus is continued. The combustion tube is ready for use when the weighed absorption train connected to the exit end for 45 minutes does not show an over-all gain in weight of more than 0.0005 g. The absorption train is then re-weighed and connected to the combustion tube.

The weighing tube is placed in a cradle hung from the pan of a balance and weighed empty. The capillary of bulb A is then dipped into the sample. By mild suction applied at the other end an amount of the sample just sufficient to fill bulb A is drawn in. The tube is then brought to the horizontal position and the ends are wiped clean and dry. It is again weighed and the difference gives the weight of the sample. After weighing, the tube is tilted and tapped lightly to transfer the liquid to bulb C. The two-holed rubber bung is now slipped on to the longer arm of the sample tube and the whole is fitted into the combustion tube as before. The nitrogen supply is connected to the sample tube and oxygen to the other inlet tube. The flow of nitrogen is started first, followed almost immediately by oxygen. The flow of nitrogen is adjusted so that the sample evaporates smoothly and the oxygen flow is set at 150 ml per minute. For liquids with a low vapour pressure at ordinary temperatures, the flow of nitrogen is increased and, if necessary, the first furnace is drawn over the sample tube and switched on. The temperature is adjusted to about  $30^{\circ}$  to  $50^{\circ}\text{C}$  below the boiling-point of the liquid. With a little practice, evaporation and combustion can be carried out smoothly. In about 30 to 35 minutes the whole of the volatile portion of the sample evaporates. If any residue remains in the sample tube, the temperature of the first furnace is raised rapidly to  $500^{\circ}\text{C}$ , the flow of nitrogen stopped and the oxygen supply connected to the sample tube. In about 5 minutes the whole of the carbonaceous matter vanishes. The tube is flushed for a further 5 minutes with oxygen at the increased rate of 250 ml per minute. The absorption tubes are then detached and left to cool. One precaution to be observed is that, when the evaporation of the sample is carried out at an elevated temperature, the exposed portion of the combustion tube between the first and second furnaces should be kept heated to a temperature above the boiling-point of the liquid, so that no condensation takes place in this region. This can be done either by wrapping the exposed portion of combustion tube with a heating tape or by playing a small flame on it.

During cooling, the pressure in the absorption tubes falls below atmospheric. Therefore, after being wiped clean, the tubes are opened momentarily to the atmosphere to equalise the pressures. They are then weighed. The gain in weight of the anhydrous tube gives the water, and the combined gain of the Midvale and guard tubes gives the carbon dioxide formed. From these weights carbon and hydrogen are calculated. A correction to the hydrogen figure is required if moisture is present in the sample.

#### RESULTS

Some of the results obtained by using the proposed method are shown in Table I. It can be seen that for pure compounds the determined results compare very well with the theoretical. For hydrocarbons, such as kerosine and decahydronaphthalene, it is not possible to deduce theoretical values, as impurities are present in the sample, but in these instances the sums of the carbon and hydrogen contents are very nearly 100 per cent.

TABLE I  
ANALYSIS OF HYDROCARBONS BY THE PROPOSED METHOD

Sample	Carbon		Hydrogen		Sample	Carbon found, %	Hydrogen found, %	
	found, %	theoretical, %	found, %	theoretical, %				
Benzene ..	92.23	92.26	7.77	7.74	Kerosine	85.70	14.35	
	92.25		7.74			85.59	14.38	
	92.25		7.41			85.57	14.34	
	92.39		7.79			87.78	12.31	
Toluene ..	91.26	91.26	8.81	8.74	Decahydronaphthalene	87.88	12.30	
	91.18		8.81			87.54	11.61	
	91.22		8.77			87.47	11.62	
Xylene ..	90.31	90.50	9.55	9.50	Neutral oil	H134	87.00	12.96
	90.38		9.69			H132	86.88	13.03
<i>n</i> -Heptane ..	84.65	84.50	15.54	15.50		H133(B)	87.12	12.30
	84.59		15.61				87.28	12.26
<i>cyclo</i> Hexane ..	85.70	85.63	14.33	14.37		H134(B)	88.08	11.71
	85.55		14.31				88.06	11.79
	85.88		14.47			H133	88.06	12.10
	85.61		14.36			H132(A)	87.92	12.12
							87.08	12.91
							86.96	13.05

We thank the Director, Central Fuel Research Institute, for his encouragement and kind permission to publish this paper.

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## The Determination of Copper in Sea Water, Silicate Rocks and Biological Materials

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The use of 2:2'-diquinoyl in *n*-hexanol as a specific reagent for the extraction and spectrophotometric determination of copper in sea water is recommended. The colour of the cuprous-diquinoyl complex can be stabilised by means of hydroquinone. The method gave a coefficient of variation of 2.5 per cent. with sea water containing 27.0  $\mu\text{g}$  of copper per litre. The method has also been used for the determination of small concentrations of copper in silicate and carbonate rocks and in biological materials. The U.S. Geological Survey granite G1 and diabase W1 have been found to contain  $15.9 \pm 0.4$  and  $121 \pm 3$  p.p.m. of copper, respectively.

COPPER is an important trace constituent of sea water, in which it occurs in amounts variously reported as in the range 0.01 to 0.47  $\mu\text{g}$ -atom of copper per litre. Chow and Robinson<sup>1</sup> have reviewed the literature published up to 1952 on the occurrence and determination of copper in sea water. It is probable that all the earlier and much of the later published work is

unreliable, owing to either faulty analytical techniques or contamination of the samples by the sampling apparatus or storage vessels. Such effects must be the explanation of the very high copper contents reported by certain workers.

Most of the published data are for surface waters, and, although they are of value in biological studies, they give little idea of the copper content of deep ocean water.<sup>2</sup> Copper is strongly concentrated by certain marine organisms and organic detritus, and this adsorption can cause considerable local variations in its concentration in sea water. Atkins<sup>3</sup> has found a regular annual cycle for copper in the surface waters of the English Channel. Copper occurs in haemocyanin, the respiratory pigment of the blood of many marine invertebrates, which is analogous to the haemoglobin of the blood of mammals. It plays an essential part in the setting of oysters and acts as an oxidation catalyst in certain enzyme systems.

In the course of geochemical studies in these laboratories of the inter-relationships of copper in sea water, marine sediments and marine organisms, a sensitive and specific method for its determination was required. The concentration of copper in sea water is too small to be determined directly, and in most of the more recent investigations it has been separated by solvent extraction with either dithizone<sup>4,5</sup> or sodium diethyldithiocarbamate<sup>1,6,7</sup> and then determined photometrically. Both these reagents are extremely sensitive, but neither is specific for copper; by the use of suitable masking agents<sup>8,9</sup> they can be made more selective.

Within the last decade, a number of reagents specific for copper have been introduced, mainly based on 1:10-phenanthroline<sup>10,11,12,13</sup> and 2:2'-diquinolyl.<sup>14,15,16,17,18,19</sup> These compounds react with monovalent copper to form strongly coloured cationic complexes that are soluble in certain organic solvents.

#### EXPERIMENTAL

In order to obtain a reasonably sensitive and completely specific method for the determination of copper in sea water, the use of 2:2'-diquinolyl was investigated. This reagent has been used for the determination of copper in natural waters,<sup>20,21</sup> which are generally at least one order of magnitude richer in copper than is sea water. Its sensitivity for copper is about two-thirds of that of most of the substituted phenanthrolines, but it is cheaper and more easily obtainable. The majority of investigators have used isoamyl alcohol as the solvent for diquinolyl, although trichloroethanol has also been used.<sup>21</sup> In order to obtain sufficiently high optical densities, large volumes of sea water (up to 1 litre) must be taken for analysis, and it was apparent that isoamyl alcohol (solubility 2.67 g per 100 ml at 22° C) was too soluble to be used for the extraction in this instance. Several other solvents were tested and it was found that *n*-hexanol (solubility 0.5 g per 100 ml) was a suitable solvent for the extraction of the cuprous-diquinolyl complex from sea water.

The optimum conditions of pH for the extraction of the cuprous-diquinolyl complex with *n*-hexanol were next investigated. Aliquots of distilled water (300 ml) were enriched with 10 µg of copper and 5 ml of 25 per cent. hydroxylamine hydrochloride solution were added, and then the solution was adjusted to the desired pH with sodium acetate and acetic acid. A double extraction with two 5-ml portions of 0.03 per cent. diquinolyl solution was then carried out. The optical density of the combined organic extracts was measured at 540 mµ in a 4-cm cell. It was found that below pH 2.7 practically no copper was extracted, but, above pH 4.0, copper was completely extracted, and in all subsequent work extractions were made at a pH between 4.3 and 5.8.

The efficiency of diquinolyl for the extraction of copper, in common with that of many other organic complexing agents, decreases markedly with the copper concentration. Hence, although 1 p.p.m. of copper can be extracted with 99 per cent. completeness by a single extraction, at a level of 0.01 p.p.m., two extractions are necessary to separate 97 per cent. of the element. For the determination of copper in sea water, three extractions with 8, 3 and 3 ml of diquinolyl reagent were used and gave over 99 per cent. recovery of added copper. In order to ensure that all the remaining copper was in the cuprous state, more hydroxylamine hydrochloride solution was added before the second extraction.

In the early stages of this work, with small amounts of copper, fading of the colour of the cuprous-diquinolyl complex was troublesome. The optical densities of the solutions sometimes decreased by as much as 3 per cent. per hour; fading was even more rapid in sunlight. Analogous fading has been encountered with cuprous-phenanthroline derivatives<sup>11</sup> and is attributed to oxidation of the complexes by atmospheric oxygen. This

oxidation can be completely prevented by the addition of 0.5 ml of 1 per cent. hydroquinone solution to the *n*-hexanol extracts.

Guest<sup>22</sup> has used diquinolyl for the determination of copper in rocks. Almond<sup>23</sup> claims coefficients of variation of about 16 and 6 per cent., respectively, for field and laboratory methods for the determination of copper in rocks in the range 38 to 300 p.p.m. In Almond's procedure the copper in the sample is brought into a soluble form by fusion with potassium pyrosulphate and then determined with diquinolyl. We have found that appreciably higher results were obtained if silicate rocks were opened up by digestion with hydrofluoric and nitric acids instead of by pyrosulphate fusion. This is probably because the fusion process attacks only the sulphide and oxide minerals, if any, in the samples, and will not dissolve copper contained in the silicate lattice. In the work described, complete dissolution of the copper, whatever its mode of combination, has been ensured by evaporating the rock sample to dryness with a mixture of hydrofluoric and nitric acids. The residue is then fused with potassium bisulphate, which also helps to free the residue from nitrate and fluoride.

#### METHOD

All solutions and aqueous reagents should be prepared with water that has been distilled from an all-glass or silica still.

#### REAGENTS—

**Diquinolyl reagent**—Dissolve 0.03 g of 2:2'-diquinolyl in 100 ml of *n*-hexanol that has been redistilled from sodium hydroxide.

**Hydroxylamine hydrochloride solution**—Dissolve 25 g of analytical-reagent grade hydroxylamine hydrochloride in about 80 ml of water, filter and dilute to 100 ml. If appreciable amounts of copper are present in the reagent, extract it with 10-ml portions of a 0.01 per cent. solution of dithizone in carbon tetrachloride until there is no change in the colour of the dithizone. Extract the solution with carbon tetrachloride until all colour has been removed.

**Sodium acetate buffer solution, N**—Prepare a solution containing 136 g of sodium acetate trihydrate per litre. If the reagent contains more than a trace of copper, extract with dithizone as described above.

**Ethanolic hydroquinone solution**—Prepare a 1 per cent. w/v solution of hydroquinone in redistilled ethanol.

**Standard copper solution**—Weigh 0.1 g of Specpure or electrolytic copper into a silica basin. Dissolve it in 3 ml of concentrated nitric acid, add 1 ml of concentrated sulphuric acid and evaporate under an infra-red heater until dense white fumes are evolved. Allow to cool and then dissolve the residue in distilled water and dilute to 100 ml. This solution, which contains 1 mg of copper per ml, is used for the preparation of the working solutions, which contain either 2 or 10  $\mu$ g of copper per ml and should be prepared freshly as required.

#### TREATMENT OF APPARATUS—

Clean the digestion flasks and the separating funnels that are to be used for the extraction of the cuprous-diquinolyl complex by setting them aside overnight filled with a (1 + 1) mixture of concentrated nitric and sulphuric acids. Empty them and rinse several times with distilled water.

#### PROCEDURE FOR DETERMINING COPPER IN SEA WATER—

Filter the sample through a No. 5 sintered-glass funnel. Transfer 900 ml of the filtrate to a 1-litre separating funnel and add 5 ml of 25 per cent. hydroxylamine hydrochloride solution and 10 ml of N sodium acetate buffer solution. Shake the solution with 8 ml of diquinolyl reagent for 5 minutes and then allow the phases to separate. Run the lower aqueous layer into another separating funnel, add 2 ml of 25 per cent. hydroxylamine hydrochloride solution and re-extract for 3 minutes with a further 3 ml of diquinolyl reagent. Separate the aqueous phase and again extract with 3 ml of diquinolyl reagent. Combine the *n*-hexanol extracts in a 10-ml calibrated flask containing 0.5 ml of 1 per cent. ethanolic hydroquinone solution and dilute to the mark with *n*-hexanol. Measure the optical density of the solution at 540  $m\mu$  in a 4-cm cell. Determine the reagent blank in the same manner with water distilled from a silica still. Prepare a calibration curve with 10 and 20  $\mu$ g of copper added to 900 ml of metal-free water.

## PROCEDURE FOR DETERMINING COPPER IN SILICATE ROCKS—

Weigh accurately 0.6 to 1 g of the finely powdered rock into a platinum crucible. Add 2 ml of concentrated nitric acid, 15 ml of 40 per cent. hydrofluoric acid and set the covered crucible aside overnight on a water bath. Evaporate to dryness on a water bath. Fuse the residue with 1.5 to 2 g of fused potassium bisulphate at dull red heat for 5 minutes. Dissolve the fused cake by warming on a water bath with 100 ml of water containing 1.5 ml of concentrated hydrochloric acid. When cold, transfer the solution to a 250-ml calibrated flask and dilute to the mark with water. Transfer 100-ml aliquots of the solution (not more than 80  $\mu\text{g}$  of copper) to 250-ml separating funnels, and add 2.5 ml of 25 per cent. hydroxylamine hydrochloride solution and 25 ml of *N* sodium acetate buffer solution. Carry out the extraction of copper as described previously for sea water, but use 6, 2.5 and 2 ml of diquinolyl reagent for the three extractions. Combine the three extracts in a 10-ml calibrated flask containing 0.5 ml of 1 per cent. ethanolic hydroquinone and dilute to the mark with *n*-hexanol. Measure the optical density of the extract at 540  $m\mu$  in a cell of suitable length (1 or 4 cm). Determine the reagent blank in the same manner, but omit the sample. Prepare a calibration curve by using 0, 5, 10, 25 and 50  $\mu\text{g}$  of copper.

## PROCEDURE FOR DETERMINING COPPER IN CARBONATE ROCKS—

Weigh 5 g of the carbonate sample into a silica flask. Dissolve it by gradual addition of 30 ml of 4 *N* nitric acid. If foam tends to rise to the top of the flask it can be broken by the addition of a drop of octyl alcohol. Cautiously evaporate the solution to dryness on a hot-plate; if organic matter is present, add 10 to 15 ml of concentrated nitric acid and repeat the evaporation. Evaporate the residue twice to dryness with 15 ml of concentrated hydrochloric acid to remove nitric acid. Dissolve the residue in 100 ml of distilled water containing 1.5 ml of concentrated hydrochloric acid and dilute to 250 ml. Carry out the determination of copper in a 100-ml aliquot as described for silicate rocks.

## PROCEDURE FOR DETERMINING COPPER IN BIOLOGICAL MATERIALS—

Weigh 0.5 to 3 g of the sample (1 to 40  $\mu\text{g}$  of copper) into a 150-ml silica conical flask, add 10 to 15 ml of concentrated nitric acid and heat the flask carefully on a hot-plate. If the reaction becomes violent, the flask should be removed from the heat source and heating resumed only when the reaction has moderated. Repeat the evaporation with 10 to 15-ml portions of nitric acid until the residue is free from organic matter. Add 2 ml of 60 per cent. perchloric acid and evaporate until dense white fumes are evolved. Dissolve the residue in distilled water, filter, and determine copper in the filtrate as described for silicate rocks. Carry out a blank determination in the same manner, but omit the sample.

TABLE I  
DETERMINATION OF COPPER IN WATER

Weight of copper present, $\mu\text{g}$	Mean optical density*	Optical-density increment per $\mu\text{g}$ of copper
2	0.080	0.0400
4	0.160	0.0400
6	0.235	0.0392
8	0.310	0.0388
10	0.385	0.0385
12	0.480	0.0400
16	0.640	0.0400
20	0.797	0.0398
25	0.985†	0.0394
30	1.185†	0.0395
50	1.920†	0.0385
70	2.680†	0.0383
100	3.840†	0.0384
		Mean 0.0393

\* Measured in 4-cm cell, less reagent blank of 0.060.

† Measured in 1-cm cell, calculated for 4-cm cell.

## BEER'S LAW AND REPRODUCIBILITY OF RESULTS

Various amounts of copper from 2 to 100  $\mu\text{g}$  in 500-ml aliquots of redistilled water were extracted in duplicate, as described for sea water (p. 301). The optical densities of the

extracts were measured at 540 m $\mu$  in 1 or 4-cm cells as appropriate. The results, which are given in Table I, indicate that Beer's law is obeyed up to at least 10 p.p.m. of copper in the *n*-hexanol phase. The molecular extinction coefficient calculated from the average slope is  $6160 \pm 109$ .

#### DISCUSSION

##### INTERFERENCE—

The possible interference of several ions has been investigated by carrying out copper determinations on 250-ml aliquots of redistilled water containing these ions. No interference was experienced with 50-mg amounts of sodium, potassium, magnesium, calcium, strontium, barium, aluminium, iron, manganese or titanium, or with 50- $\mu$ g amounts of bismuth, cadmium, cobalt, chromium, gallium, lead, mercury, nickel, thallium, silver or zinc. Complete recoveries of 10  $\mu$ g of added copper were obtained in the presence of 1 mg of phosphorus, as phosphate, 1 mg of silicon, as silicate, and 1 mg of fluorine, as fluoride. No interference can therefore be expected from any of these ions at the concentrations at which they occur in sea water or silicate rocks.

##### APPLICATION OF THE METHOD TO SEA WATER—

It was found that the proposed method was not subject to salt error, since the optical-density increment per  $\mu$ g of added copper was the same whether the extraction was from sea water or distilled water.

The reproducibility of the method was tested by carrying out six replicate analyses on a sample of surface water collected from the Irish Sea in January, 1956. Before analysis, the water (chlorinity = 18.83 ‰) was filtered through a No. 4 sintered-glass filter. The results (26.0, 26.6, 27.0, 27.0, 27.4 and 28.0; mean 27.0  $\mu$ g of copper per litre) showed a coefficient of variation of 2.5 per cent. Similar reproducibility was obtained with a sample of water from the English Channel (chlorinity = 19.36 ‰) containing 19.0  $\mu$ g of copper per litre.

##### ACCURACY OF THE METHOD FOR SILICATE ROCKS—

In order to test the accuracy of the proposed method, six replicate analyses were carried out on a granite G1 from Westerly, Rhode Island, and on a diabase W1 from Centerville, Virginia. These rocks, which were obtained from the U.S. Geological Survey, have been used as the basis of a collaborative study<sup>24,25</sup> of the precision of methods for the determination of major and minor components in silicate rocks. Ahrens<sup>26</sup> has summarised the results, both spectrographic and chemical, obtained for these rocks. The figures for copper show very poor reproducibility, the results ranging from 5 to 20 p.p.m. for G1 and from 44 to 130 p.p.m. for W1. Ahrens recommends values of 11 and 110 p.p.m., respectively, as the most probable concentrations, but states that the former figure may need considerable revision because of poor agreement.

The proposed method showed the presence of 15.9 p.p.m. of copper in G1 and 121 p.p.m. in W1 (coefficients of variation 2.5 and 3.5 per cent., respectively). These figures are of the same order as those recommended by Ahrens, but are somewhat higher in both cases. As a further check on the reproducibility of the method, a gabbro from Colmonell, Ballantrae, was analysed; the average of sixteen determinations showed a copper content of  $29.8 \pm 1.1$  p.p.m. (coefficient of variation 3.5 per cent.).

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## Use of the Wide-bore Dropping-mercury Electrode for Long-period Recording of Concentration of Dissolved Oxygen

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A new type of dropping-mercury electrode, consisting of a capillary of 0.8 mm internal diameter, sloping upwards, which is stable in performance over long periods, has been used for recording the concentration of dissolved oxygen in natural waters for periods of weeks. One form of the equipment records dissolved oxygen directly in parts per million, thermistors in a non-electronic circuit compensating for the effect of any change in water temperature. The range is 0.0 to 15.0 p.p.m. by weight, and the mean value of the errors in two field trials was 0.00 p.p.m., taking into account the signs of the errors; the standard deviation of their distribution about this mean was 0.06 p.p.m. The method can be used either with the water flowing past the electrode or with stationary samples down to 1 ml.

In studies of the respiration of tissues or invertebrate animals, and the de-aeration and re-aeration of polluted rivers, it is often useful to have a continuous record of the concentration of dissolved oxygen. The proposed method is being used for rivers and effluents and its use is now being extended to laboratory applications, including direct recording of the concentration of dissolved oxygen in samples as small as 1 ml.

No review appears to exist of instrumental methods of indicating and recording concentrations of dissolved oxygen, so perhaps a very brief selective survey of the field will be useful.

### SURVEY OF METHODS

#### METHODS IN WHICH ELECTRODES ARE NOT USED—

One method<sup>1</sup> depends on removal of the oxygen from the water by means of an inert gas, and determination of the oxygen content of the resulting gas mixture by the paramagnetic method; the equipment is complex and requires mains power. The same disadvantages are present in a mechanised version<sup>2</sup> of the Winkler chemical determination.

#### METHODS IN WHICH ELECTRODES ARE USED—

It appears that all the electrode methods measure the current permitted to flow by the reduction of oxygen to hydrogen peroxide or to water. These can be sub-divided into methods in which a solid metal electrode is used and those in which a mercury electrode is used.

**Solid electrodes**—Solid electrodes have been used for the determination of dissolved oxygen by workers in bacteriology,<sup>3,4,5,6</sup> biochemistry<sup>7,8</sup> and physiology,<sup>9,10,11,12,13</sup> and have been applied also to the determination of dissolved oxygen in natural waters<sup>14,15,16</sup> and boiler-feed water.<sup>17</sup> In general, solid electrodes require frequent re-calibration, and, when used in natural waters, they tend to become coated with calcium carbonate.

**Mercury electrodes**—A mercury electrode has a great advantage over a solid electrode in that it is easy to arrange for its surface to be renewed automatically, as, for example, the use in ordinary polarography of the dropping-mercury electrode. Dissolved oxygen in natural waters and other aqueous liquids has been measured in this way by many workers, including Seaman and Allen,<sup>18</sup> Rand and Heukelekian,<sup>19</sup> Moore, Morris and Okun<sup>20</sup> and Ingols.<sup>21</sup> The impression given in the literature is that dissolved oxygen can be measured satisfactorily by the usual type of dropping-mercury electrode if it is re-calibrated frequently; for example, Seaman and Allen<sup>18</sup> recommend that the calibration should be checked several times a day. All the authors mentioned used a standard reference electrode as their second electrode, but Foyn<sup>22</sup> used a dropping-mercury electrode with a second electrode consisting of a zinc plate immersed in the water; again, the calibration was checked before each test. Ambuhl<sup>23</sup> renewed the mercury surface by means of a motor-driven wiper, new mercury flowing from a reservoir to replace that wiped away.

## EXPERIMENTAL

### UNSUCCESSFUL USE OF SOLID ELECTRODES—

When a stationary gold electrode was used in conjunction with a saturated-calomel electrode, currents produced by dissolved oxygen in 0.1 *M* potassium chloride solution decreased with time. During this experiment the gold electrode became covered with a film, probably of mercury from the calomel electrode. Use of a guard electrode, as described by Giguere and Lauzier,<sup>14</sup> to avoid this deposition of mercury did not prevent the fall in current, which also occurred when a stationary platinum electrode was used with cadmium as the second electrode.

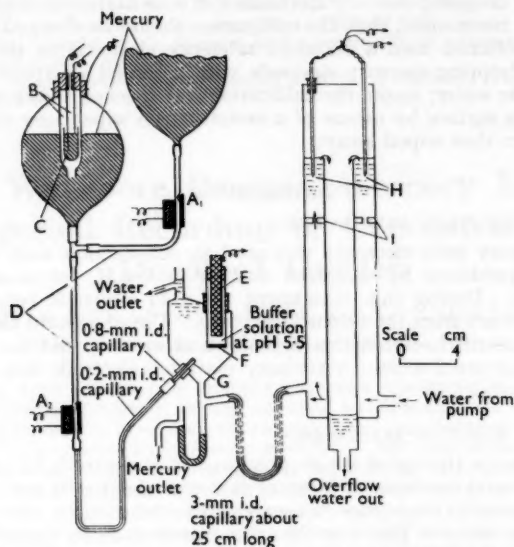
### SUCCESSFUL USE OF MERCURY ELECTRODE—

First experiments on the use of the dropping-mercury electrode for oxygen measurement were with a conventional electrode of internal diameter about 0.04 mm and pointing downwards, which was placed in Stevenage tap-water and connected by way of a microammeter to a zinc plate in the water. This was the arrangement used by Foyn<sup>22</sup>; we found it gave an almost linear relationship between current and concentration of dissolved oxygen in parts per million if the temperature was kept constant. This electrode, however, would not behave consistently for more than a few hours, as the drops became smaller and more frequent, and finally ceased altogether. This is not uncommon with the conventional dropping-mercury electrode and may be more liable to occur in the proposed application, owing to the tendency for calcium carbonate to deposit in or near the very fine bore of the electrode. After many such failures, it seemed to be clear that this form of electrode would not be capable of giving a stable performance if left in continuous operation over a period of days or weeks.

This mechanical failure of the conventional dropping-mercury electrode may well have been due to its very narrow internal diameter; trials were therefore made with capillaries of bore between 0.4 and 1.05 mm. It was found to be best to arrange these capillaries so that they delivered mercury upwards to the orifice through which mercury enters the solution. The first successful arrangement was to point the wide-bore capillary vertically upwards with a bevel ground at 45° to the horizontal, but it proved to be equally successful to point the wide-bore capillary upwards at about 45° to the horizontal (see Fig. 1). Although all the capillaries in the stated range of internal diameters gave completely stable behaviour, we standardised early on the range 0.8 to 1.0 mm; a number of such electrodes has been in intermittent use, for periods of weeks' continuous operation at a time, for over a year, and none has ever altered in behaviour or calibration, in spite of our practice of the re-use of mercury after simple chemical cleaning and drying, without distillation. At present, a wide-bore dropping-mercury electrode made of Perspex is on trial, and it appears to be as satisfactory as the glass ones.

A problem to be solved was to find means of regulating the flow of mercury to these wide-bore capillaries, which, unlike the conventional dropping-mercury electrode, do not provide any significant restriction to flow. One method is to include a capillary restriction between the reservoir of mercury and the electrode. At first it was thought that this additional capillary would itself have to be of rather wide internal diameter and the results were good with a head of mercury of about 15 cm and a long capillary of internal diameter

about 1 mm, but later the arrangement shown in Fig. 1 was found to be completely satisfactory, the system being to supply mercury (at a head of 15 cm) to the wide-bore electrode through a flow-restricting capillary about 25 cm long and of bore about 0.2 mm. Another system found to be satisfactory was to feed the mercury to the wide-bore electrode by means of a motor-driven Perspex syringe with piston rings of silicone rubber, which holds a 2-day supply of mercury.



- |  |                                |
|--|--------------------------------|
| A <sub>1</sub> , A <sub>2</sub> = Electromagnetic valves | E = Zinc electrode             |
| B = Platinum contacts                                    | F = No. 4 sintered-glass disc  |
| C = Glass or Perspex boat containing mercury             | G = Dropping-mercury electrode |
| D = Silicone rubber tubing                               | H = Thermistors                |
|  | I = Disc with 4 holes          |

Fig. 1. Layout of apparatus showing cell containing electrodes and systems for supplying water and mercury. All vessels are circular in section. Thermistors are omitted when temperature compensation is not required

Besides its reliability, another advantage possessed by the wide-bore electrode is that currents are about ten times greater than with the conventional electrode, which means that a polarographic current of about 40  $\mu$ A is produced by the reduction of dissolved oxygen in air-saturated water at about 20°C; the second electrode used in conjunction with this electrode must be capable of carrying such a current without significant polarisation.

From the consideration of a number of polarograms it was decided that the best fixed voltage to apply in order to record dissolved oxygen would be -0.5 volt with respect to the zinc electrode (equivalent to -1.5 volts with respect to the saturated-calomel electrode). Use of this voltage, which means working on the second plateau of oxygen reduction, has the advantage that cyanide and sulphide will not interfere, whereas at the more positive potential of the first plateau of oxygen reduction their oxidation waves would be present. The only other source of interference likely to be encountered is the reduction of metal ions, and in most natural waters it is unlikely that the concentrations of these, which include iron, lead, copper, zinc and nickel, will be so high as to have a significant effect. If work has to be done on solutions containing substances that interfere with the proposed method, the equipment could probably be rearranged so as to avoid error from such a cause. The suggested method of rearrangement is to use two wide-bore dropping-mercury electrodes each with its own second electrode and in its own cell; the solution under examination would be in both cells, but in one it would be de-oxygenated with a stream of electrolytically generated hydrogen, or with sodium sulphite and a catalyst. The difference between the currents from

the two cells, displayed on a single meter, would then be a measure of the concentration of dissolved oxygen.

For placing the electrodes in the sample, a wide variety of sizes and shapes of cells can be used; a type used in our work is shown in Fig. 1. For a given cell and position of electrodes the current corresponding to a given concentration of dissolved oxygen is the same with the water stationary as with it moving through the cell at velocities up to a critical value, above which the current increases somewhat with increase in velocity of the water. For the cell shown in Fig. 1 this critical value is about 40 ml per minute, and for more rapid flow the current increases only by about 0.5 per cent. of its magnitude at zero flow for each 10 ml per minute increase in flow beyond 40 ml per minute, up to a rate of flow of 220 ml per minute. As arranged in Fig. 1, the rate of flow through the cell, governed by the head of water in the constant-head unit on the right, is about 100 ml per minute, *i.e.*, the rate at which the equipment is calibrated. The constant-head unit is of the type described by Spoor<sup>24</sup>; this arrangement does not expose the water to air. In a 1-ml cell the current was unaffected by an increase in rate of flow of water from zero to 5 ml per minute, and then increased by about 0.3 per cent. of its value at zero flow for every 1-ml increase in rate of flow above 5 ml per minute.

The conductivity of the water has no effect provided its value is equal to or greater than 50 micromhos per cm cube. The pH has likewise no influence, at least within the range of pH values so far tested—5 to 8.5—and is probably without effect for pH values higher than 8, although for those much less than 5 it might be necessary to use a less negative value for the potential of the dropping-mercury electrode.

#### APPARATUS—

The layout of the apparatus is shown in Fig. 1.

**Supply of mercury**—A constant rate of flow of mercury (6 ml per hour) and a constant drop rate (1 drop every 2.5 seconds) are maintained by supplying mercury to the electrode from a reservoir in which the surface of the mercury is 15 cm above the electrode tip; the level in the reservoir is kept constant by means of platinum contacts, which cause mercury to be admitted as required through an electromagnetic valve,  $A_1$ , (Londex Ltd., type LF/VA, with 24-volt a.c. coil, but operated on 9 volts d.c.), which, until energised, clamps firmly on a silicone rubber tube (QS166 3-mm Symel sleeving, H. D. Symons Ltd.). The platinum contacts do not carry the current for the electromagnetic valve; they switch on this current by means of a type P.O.3000 relay operating on 9 volts d.c. From the reservoir, mercury flows by gravity through silicone rubber tubing that has a screw-clip or an electromagnetic valve,  $A_2$ , to stop the flow. At a level below the delivery tip of the dropping-mercury electrode, this silicone rubber tubing joins a 25-cm length of glass capillary tubing of bore about 0.2 mm bent to join, by means of poly(vinyl chloride) or polythene tubing, to the lower end of the glass capillary tubing that is the electrode. Both the 0.2-mm and the 0.8-mm capillary tubing are precision-bore Veridia capillary tubing (Chance Brothers Ltd.). As an alternative to the supply of mercury to the electrode by gravity, supply from a motor-driven syringe, as mentioned previously, has proved to be satisfactory in short-period tests. Whichever method is used to supply the electrode, the mercury can be re-used several times without distillation, simple chemical cleaning followed by drying by passage through a pin-hole in a filter-paper being sufficient.

**Reference electrode**—The zinc electrode shown in Fig. 1 is a convenient reference electrode, capable of carrying, without significant polarisation, the highest current (about 40  $\mu$ A) that will be encountered; it comprises a pure zinc rod (Imperial Smelting Corporation) in a buffer solution (*N* hydrochloric acid plus 0.2 *M* sodium acetate solution) of pH 5.5, which communicates with the water through a No. 4 sintered-glass disc. This electrode can be quickly made from a cut-down "filter-tube"; it has a potential of -1.0 volt with respect to a saturated-calomel electrode and works for at least 1 month without replacement of the buffer solution. It is possible, however, that a mercury-pool electrode, as used in commercial polarographs, would be equally satisfactory as the second electrode.

**Equipment not fitted with temperature compensation**—When temperature compensation is not required the thermistors shown in Fig. 1 are omitted, and the circuit to be used is given in Fig. 2.  $R_1$  is adjusted until *V* indicates 0.5 volt with the terminal connected to the mercury electrode the more negative one.

If all readings are taken with the water at a standard temperature, a current - dissolved oxygen calibration graph, prepared as described later, gives the concentration of dissolved

oxygen from the current shown by the indicator or recorder. Alternatively, the instrument may be calibrated directly in parts per million of dissolved oxygen with the aid of such a graph.

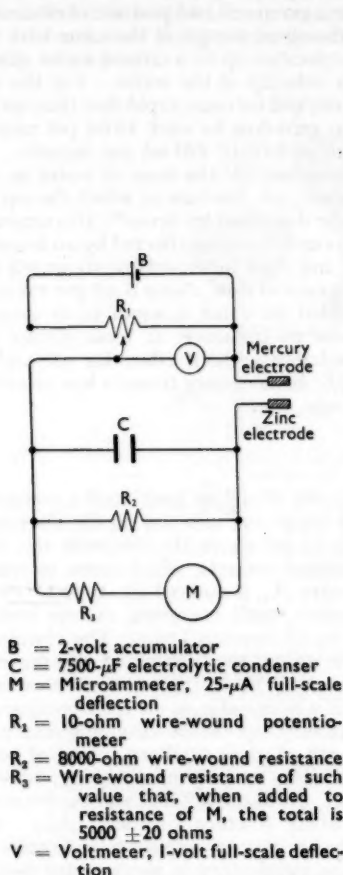


Fig. 2. Circuit for dissolved-oxygen indicator and recorder without temperature compensation

If, on the other hand, it is required to take readings with the water at other temperatures, then each measured current must be converted to its equivalent value at the standard temperature for which the calibration graph is drawn. The factor for this conversion can be obtained from a graph drawn from the following figures, which are the relative currents produced by constant concentration of dissolved oxygen at various water temperatures: 0.730 at 0° C, 0.803 at 5° C, 0.880 at 10° C, 0.952 at 15° C, 1.000 at 18° C, 1.028 at 20° C, 1.100 at 25° C, 1.171 at 30° C and 1.236 at 35° C. In our experience, these figures apply to all equipments in which the wide-bore dropping-mercury electrode is used for measurements of dissolved oxygen.

The calibration graph itself, for any desired standard temperature, can be prepared by using tap-water at this standard temperature containing known concentrations of dissolved oxygen, as determined by the Winkler chemical method.<sup>25</sup> Alternatively, tap-water at any temperature can be used, but each current has to be converted to its equivalent at the standard temperature by means of a conversion factor obtained as described above.

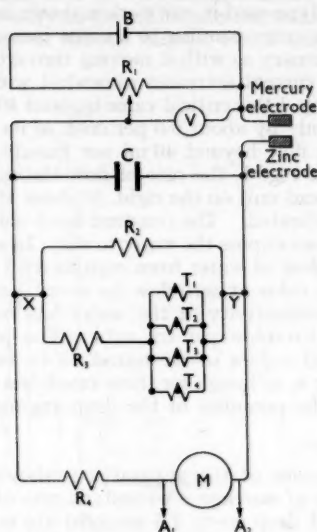


Fig. 3. Circuit for dissolved-oxygen indicator and recorder with temperature compensation

**Equipment fitted with temperature compensation**—The indicator or recorder can be marked directly in parts per million of dissolved oxygen if arrangements are made for automatic compensation for the increase in polarographic current with temperature. This compensation may be effected by the decrease in resistance, as temperature rises, of thermistors immersed in the water; the circuit is shown in Fig. 3.

The circuit values are easily arrived at by experiment. A variable resistance is connected temporarily between X and Y instead of  $R_2$ ,  $R_3$  and the thermistors. Tap-water is supplied to the electrodes at the rate of flow to be used in practice, its temperature being about midway in the range of temperatures to be covered and its concentration of dissolved oxygen being the maximum to be recorded; the variable resistance is now adjusted to give an almost full-scale reading on meter M. The variable resistance is then removed and its resistance measured.

If the resistance so measured is  $R_s$  then the required approximate value of  $R_2$  will be  $2R_s$ , whereas the thermistor, or set of thermistors in parallel, is chosen to have a resistance of somewhat less than  $2R_s$  at a temperature midway in the range; thermistors must be of a type aged by the manufacturer. The required approximate value of  $R_3$  can now be calculated from the equation—

$$R_3 = \left\{ \frac{xR_t[R_t(R_m + R_4 + R_s) - (1 + k)\{2R_s(R_m + R_4) + R_t(R_m + R_4 + R_s)\}]}{k[2R_s(R_m + R_4) + R_t(R_m + R_4 + R_s)]} \right\} - R_t$$

where  $R_m$  = the resistance of meter M in ohms,

$R_t$  = the resistance of the thermistors in ohms at a temperature midway in the range,

$R_4$  = the resistance of  $R_4$  in ohms,

$x$  = the fractional rate of increase per °C rise in temperature of the resistance of the thermistors at a temperature midway in the range, and

$k$  = the fractional rate of increase per °C rise in temperature of the current due to a given concentration of dissolved oxygen at a temperature midway in the range.

For  $k$  it is sufficiently accurate to select the value given against the nearest temperature from the following: 0.0174 at 5° C, 0.0171 at 10° C, 0.0163 at 15° C, 0.0141 at 20° C and 0.0129 at 25° C.

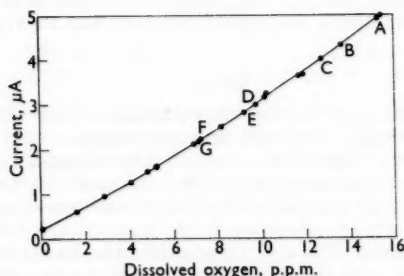


Fig. 4. Relationship between current and concentration of dissolved oxygen for a temperature-compensated recorder. The temperatures corresponding to some points on the curve are: A, 28° C; B, 1.5° C; C, 4° C; D, 2.6° C; E, 18.8° C; F, 29.9° C; G, 3.5° C

Exact values for  $R_2$  and  $R_3$  can now be found by using the circuit of Fig. 3 modified as follows: remove C, replace the electrodes by a meter having a full-scale deflection of about 50  $\mu$ A to measure the total current and replace  $R_2$  and  $R_3$  by variable resistances initially set at the respective approximate values determined as described. Immerse the thermistors in water of temperature about midway in the range to be covered, adjust the total current to, say, 35  $\mu$ A, and note the reading on meter M. Transfer the thermistors to water of temperature about the maximum in the range and adjust the total current by means of  $R_1$  to the new value it would have if the current of 35  $\mu$ A had been due to dissolved oxygen; the factor required to find the new value can be obtained from the graph of relative currents

previously described (p. 308). Adjust  $R_3$  until the original reading of meter M has been restored. Return the thermistors to the water of temperature about midway in the range, adjust the total current to 35  $\mu$ A, and adjust  $R_2$  until the original reading of meter M has been restored. Continue in this way, using also water of temperature about the minimum in the range, until the reading of M is unaltered by placing the thermistors in water at any of the three temperatures, provided that the total current is always adjusted to correspond with the temperature.

Finally, a calibration graph, of which an example is given in Fig. 4, is prepared by supplying the cell with water, at any temperature, containing known concentrations of dissolved oxygen. If desired, the scale of meter M, or the recorder charts, can be inscribed directly in parts per million of dissolved oxygen.

#### METHODS OF RECORDING

When mains power is available, the dissolved-oxygen concentration is continuously recorded on a strip-chart by using a stable d.c. amplifier of the chopper type and a recorder having a full-scale deflection of about 1 to 5 mA. Commercially available equipment or the chopper amplifier described by Davies<sup>26</sup> can be used, the circuit being modified from that published to allow rectification of the amplified current by the second pair of contacts of the high-speed relay, and to include one more stage of amplification.

On the other hand, when only a 12-volt accumulator is available for power supply, a photograph of the meter indicating dissolved-oxygen concentration is taken automatically at chosen intervals, usually every 15 minutes or every hour, by a camera that gives 200 pictures, each 1 inch square, with one loading of 35-mm film. The sequence of events begins when a clockwork time-switch energises electromagnetic valve  $A_2$  in Fig. 1, thereby starting the flow of mercury, and simultaneously starting the 12-volt immersion pump supplying the river water to the equipment and switching on the 12-volt charging unit of an electronic flash unit, as used by photographers. Three minutes later, the timing unit operates the camera shutter, which, by means of its internal synchronised contacts, fires the electronic flash tube, the light from which illuminates the oxygen-indicating meter indirectly by way of the top and sides of the box, which are painted white internally. The whole equipment then ceases to operate until the next sequence begins. Usually, the camera is arranged so that the photographs include not only the dissolved-oxygen indicator, but also the dial of a mercury-in-steel thermometer, a river-level indicator and an exposure-number counter or a battery-operated clock.

#### RESULTS

After laboratory tests had shown that the equipments held their calibrations indefinitely for tap-water, they were used in two field investigations.

The first of these was the indication, every 15 minutes, of the concentration of dissolved oxygen in a sewage effluent containing suspended and colloidal material (a switch was provided to change the method of indication to a continuous one when desired). At this time, the method of automatic compensation for water temperature had not been developed, so the temperature of the effluent was also noted when the meter was read, and the concentration of dissolved oxygen was found from these data by the procedure described. In a consecutive series of 115 check tests against the azide modification<sup>25</sup> of the Winkler method, over a period of 3 weeks, the mean value of the errors of the results given by the equipment was 0.002 p.p.m. by weight, taking account of the signs of the errors; the standard deviation of their distribution about this mean was 0.06 p.p.m. and the maximum error was 0.15 p.p.m. The range of concentrations of dissolved oxygen encountered in this investigation was 3.20 to 7.05 p.p.m., and the range of temperatures 11.6° to 19.0° C.

The second field investigation was on a small river at a point downstream of the entry of the effluent from the sewage works of a large industrial town. On this occasion there was less opportunity to make check tests, which numbered 19 over a period of 3 weeks, including 3 checks with tap-water at Stevenage where the equipment was sent by lorry—a journey of 100 miles. In this investigation, photographic recording was used and compensation for water temperature, over the range 0° to 30° C, was incorporated; readings were directly in parts per million of dissolved oxygen. The errors, calculated as above, had a mean of 0.01 p.p.m. by weight, and the standard deviation of their distribution about this mean was 0.07 p.p.m.; the maximum error was 0.20 p.p.m. In these 19 check tests,

the range of concentrations of dissolved oxygen was 2.20 to 11.00 p.p.m., and the range of temperature was 5° to 20° C.

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# Notes

## A MODIFICATION OF THE VON STIEGLITZ ELECTROMETRIC METHOD FOR SUGAR TITRATIONS

THE well known Lane and Eynon<sup>1</sup> method for the titration of reducing sugars at the boiling-point with Fehling's solution has been modified by von Stieglitz,<sup>2</sup> who determined the end-point electrometrically instead of colorimetrically. This has some advantages when the colour of the solution being titrated masks the methylene blue end-point, or when the titration is carried out in unsuitable lighting conditions. In ideal conditions, some operators experience difficulty in detecting the methylene blue end-point.

The von Stieglitz method is not well known in this country, as it was described in a journal that is not readily accessible, although it has also been mentioned by Browne and Zerbán.<sup>3</sup> This method requires the preparation of a special electrode that has a porous plug of plaster of Paris in the end. The useful life of these plugs is rather short. We have found that the von Stieglitz electrode can be replaced with advantage by the outer case of a Cambridge pH reference electrode, or one of a similar type. The Cambridge electrode has a ground-glass sleeve that permits electrical contact to be maintained between the inside and the outside of the electrode.

The apparatus is shown in Fig. 1. The copper wires should be cut from the same roll of 1-mm diameter pure copper wire, and they should be kept clean with fine emery cloth. The sensitive galvanometer has a central zero-point and a sensitivity of about 2  $\mu$ A per division. The von Stieglitz solution used for filling the Cambridge electrode is prepared by mixing 5 ml of Fehling's solution No. 2 (alkaline tartrate), 5 ml of sodium sulphate solution (39.4 g of the anhydrous salt per litre) and 20 ml of distilled water. This solution is suitable for titres of between 15 and 30 ml, but it is preferable to use 40 ml of distilled water if the titres lie between 30 and 50 ml.

The sugar solution is titrated against mixed Fehling's solution in the usual manner, the end-point being reached when the null-point is recorded on the galvanometer. As the sugar solution is added, the deflections of the needle become less and less; they are not detectable at

the end-point, and, finally, a deflection in the opposite direction is given when the end-point is passed.

Differences in titre between this method and the methylene blue indicator method have never exceeded 0.1 ml in 25 ml with any of the sugars mentioned in the Lane and Eynon Tables.

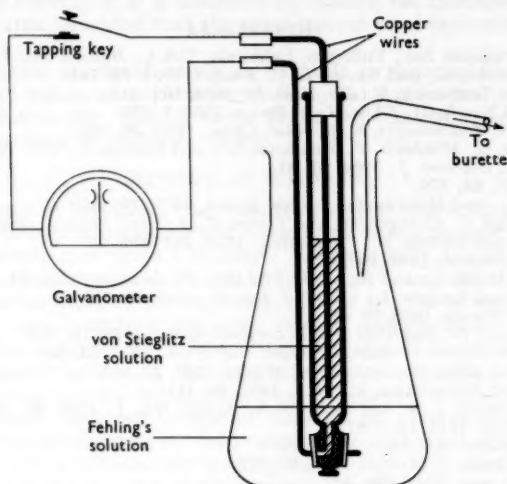


Fig. 1. Apparatus for the modified von Stieglitz electrometric method for sugar titrations

It is advisable for each analyst to check the Lane and Eynon Tables for his own conditions. The simplest way of doing this is to follow the method of Zerban, Hughes and Nygren.<sup>4</sup>

A constant-volume method discussed in the Proceedings of the International Commission for Uniform Methods of Sugar Analysis<sup>5</sup> makes it possible to dispense with the use of tables. The electrometric method of end-point detection could be applied to this procedure with suitable checks against a standard invert sugar solution. Correction for variable sucrose is still necessary.<sup>6,7</sup>

We thank the Directors of Spillers Limited for permission to publish this Note.

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SPILLERS CENTRAL LABORATORY  
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#### THE DETERMINATION OF WATER IN GLYCEROL, MARGARINE, OILS AND FATS

A METHOD is described for the determination of water in glycerol, margarine, oils and fats. It involves the use of an apparatus that permits a thin film of material to be heated in a vacuum, and the loss in weight is calculated as water.

In July, 1956, the Karl Fischer method for the determination of water was adopted by the British Standards Institution in place of the International Standards Method of 1911. The latter was generally referred to as the vacuum-desiccator method. The use of concentrated sulphuric acid and the time required to attain constant weight were two disadvantages of the vacuum-desiccator method.

The object of this investigation was to find a method that would be suitable as an alternative to the Karl Fischer and be less expensive and more simple in operation.

Heidbrink<sup>1</sup> published an article entitled "Plate Glass Apparatus as a Simple Tool for the Rapid Determination of Water and Other Volatile Material in Emulsions and Viscous Mixtures." A similar method adopted for cosmetics by Iwasenko and Kraus<sup>2</sup> includes the use of low temperatures, small samples and relatively large surface areas, which permit water to evaporate easily. Heidbrink used two flat glass plates resting in a cradle to which was attached a hook. The sample was placed on the lower plate and covered immediately with the top plate. The two plates were rubbed together to make the sample spread into a thin film, and moisture was determined by evaporation in an air-oven.

By using these investigators' findings as a background, it was found to be necessary in the development of the method to take certain precautions in order to avoid loss of glycerol during heating and to eliminate errors caused by the hygroscopic nature of glycerol. Loss of glycerol was completely avoided by adopting the use of a vacuum-oven. Errors caused by absorption of moisture from the atmosphere were eliminated by completing the determination without delay. The effects of various temperatures, times of heating and also weights of sample were investigated to ascertain the correct conditions for the determination.

#### METHOD FOR GLYCEROL

##### APPARATUS—

The apparatus is similar to that used by previous workers,<sup>1,2</sup> but is made of aluminium and weighs about 20 g. The two plates are approximately 3 inches in diameter and the lower one has a rim to prevent the glycerol from creeping over the side (see Fig. 1).

##### PROCEDURE—

Drop on to the lower plate of the apparatus 0.35 to 0.45 g of the sample, place the top plate over the lower plate immediately and rub them together. Fix the two plates in the cradle provided, and weigh quickly and accurately to 0.0001 g. Transfer to a vacuum-oven kept at a temperature of 58° C and lift the top plate on to the hook of the cradle. Evacuate the oven. Leave the sample for at least 5 hours, maintaining a vacuum of -27 inches of mercury throughout. Release the vacuum, replace the top plate of the apparatus on the lower and transfer from the oven to a desiccator. When cool, weigh as soon as possible and note the loss in weight. Calculate the percentage of water in the sample.

The conditions stated must be strictly observed in order to produce satisfactory results.

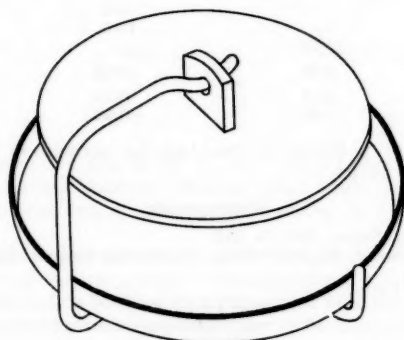


Fig. 1. Apparatus for determining water

#### RESULTS

The results were compared with those by the Karl Fischer method and also those by subtracting from 100 per cent. the sum of the glycerol and total residue at 160° C found by analysis. A comparison of the these results is shown in Table I.

TABLE I

COMPARISON OF THE RESULTS OF THE DETERMINATION OF WATER BY DIFFERENT METHODS

Sample	Water found by Karl Fischer method,	Water found by subtracting from 100 per cent. the sum of the glycerol and total residue at 160° C,	Water found by proposed method,
	%	%	%
Crude glycerol ..	4.82, 4.94, 5.09, 4.93	4.87	4.70, 4.68, 4.61, 4.93, 4.93
	5.11, 5.24	5.01	4.72, 5.17
	5.04, 4.92, 5.03, 4.82	4.66	5.05, 4.83
	4.71	4.86	4.81, 4.75
	—	5.02	4.81, 5.07, 5.14, 4.74, 4.74
	4.84	4.77	4.58, 4.85, 4.68, 4.52
Pure glycerol ..	5.13	5.03	5.11, 5.11, 5.06, 5.17, 5.15
	9.90	—	10.05, 10.09

## APPLICATION OF THE METHOD TO MARGARINE, OILS AND FATS

The foregoing investigation and procedure for the determination of water in glycerol were applied to margarine, oils and fats. With the following modifications, the method can be adopted for these materials also—

- (a) weigh accurately 1.75 to 2.0 g of sample,  
 (b) place for 1 hour in a vacuum-oven maintained at 70° C.

Some results obtained on margarine, oils and fats are shown in Table II.

## CONCLUSIONS

The method described has the advantages that (a) no great skill is required, just accuracy and care by the operator, (b) the apparatus is simple and easy to clean, (c) only a small amount of manipulative work is required, and (d) the determination is complete in a short time, *i.e.*, 6 hours for glycerol and 1 hour for margarine, oils and fats.

TABLE II

COMPARISON OF THE RESULTS OF THE DETERMINATION OF WATER BY DIFFERENT METHODS

Sample	Water found by Dean and Stark method, <sup>a</sup>	Water found by heating in an oven, <sup>a</sup>	Water found by proposed method,
	%	%	%
Margarine .. ..	—	15.3	15.42, 15.46
	—	15.0	15.55, 15.31
	10.25	—	10.11, 9.95
Lard acid oil ..	3.40	3.52	3.44, 3.50
Tallow .. ..	0.70	0.98	0.79, 0.85
	0.90	0.96	1.11, 0.99

I thank the Directors of J. Bibby & Sons Ltd. for permission to publish this Note, and also Mr. Weatherall for his advice.

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ANALYTICAL DEPARTMENT

J. BIBBY &amp; SONS LTD.

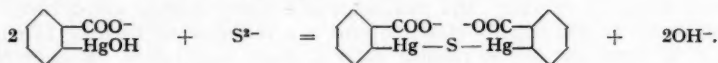
GREAT HOWARD STREET  
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## THE ANALYTICAL APPLICATION OF ORGANIC MERCURY COMPOUNDS

ORGANIC mercury compounds of the type  $R\text{-HgOH}$  can form complexes with thiourea, xanthates, mercaptans and compounds that form ions such as  $S^{2-}$ ,  $S_2^{2-}$ ,  $CS_3^{2-}$  and  $CS_4^{2-}$ . This property can be used analytically for the determination of these types of sulphur-containing compounds.

For titration in aqueous solutions, only water-soluble organic mercury compounds can be used, *i.e.*, those that have phenolic or carboxylic functions and are soluble in alkaline solution. The complexes formed are also soluble in water, and, in the presence of a suitable indicator, a titration is possible. To date, the following compounds have proved to be suitable indicators: sodium nitroprusside, diphenylcarbazone, dithizone, monomercurphenolphthalein, thiofluorescein and certain products that result from the heating of organic compounds with sulphur. If the appearance of the complex is sufficiently distinct, as occurs when dimercurfluorescein is used, an indicator is unnecessary. By choosing a suitable indicator it is possible to titrate one sulphur compound in the presence of another, *e.g.*, sulphide can be determined in the presence of xanthates when dithizone is used as indicator, but, when diphenylcarbazone is used, the titre agrees with the total amount of sulphide *plus* xanthate present. In some instances the titre depends also on the indicator used, *e.g.*, in the titration of sulphide with a clear 0.002 to 0.05 *M* solution of *o*-hydroxymercurbenzoic acid in 0.2 *N* potassium hydroxide, a freshly prepared 0.1 per cent. solution of dithizone in ethanol being used as the indicator.

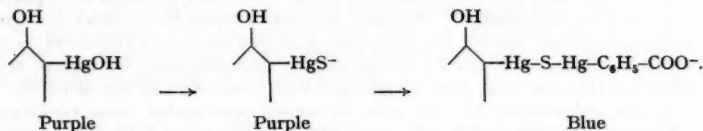
One millilitre of indicator solution and 5 ml of *N* potassium hydroxide are added to 100 ml of water containing from 50 to  $2 \times 10^4$   $\mu\text{g}$  of hydrogen sulphide and the mixture is titrated with the reagent until the colour of the solution changes from yellow to a permanent purple. Under the conditions described, the end-point is sensitive to 0.15 ml of 0.002 *M* *o*-hydroxymercurbenzoic acid. The titre agrees with the following reaction—



The presence of xanthates, thiourea or the ions  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{S}_2\text{O}_4^{2-}$  and  $\text{CNS}^-$  does not interfere with the titration. When sodium nitroprusside is used as indicator and the reagent is added until the purple colour of the solution disappears, the titre agrees with the reaction—



The use of monomercurphenolphthalein as indicator depends on the formation of blue-coloured mixed complexes. An alkaline solution of this compound is purple, and the addition of sulphide changes its colour only slightly. However, in the presence of compounds such as *o*- and *p*-hydroxymercurbenzoic acid, the colour distinctly changes to blue. This can be represented as follows—



The fusion of sulphur with resorcinol at 250° C, and with phenolphthalein at 280° C, produces two compounds, which, in alkaline solution, change colour when organic mercury compounds are added; the first from yellow to red, and the second, reduced by boiling with sodium sulphite, from red to blue.

An alkaline solution of thiofluorescein is blue, but it changes to very pale yellow when organic mercury compounds or mercury salts are added. Thiofluorescein can be used in the titration of mercury in alkaline potassium iodide solution to a permanent blue colour. In this way 10  $\mu\text{g}$  of mercury can be determined without interference from other cations, such as divalent copper and lead.

An interesting application of dimercurfluorescein is made possible by the fact that, in alkaline solution, it has a green fluorescence, which changes to a pinkish orange colour when any of several sulphur compounds is added. It is possible to titrate with a diluted solution of dimercurfluorescein to the first green fluorescence, and in this way from 5 to 50  $\mu\text{g}$  of hydrogen sulphide and very small amounts of many other sulphur compounds can be determined.

## THE DETERMINATION OF SMALL AMOUNTS OF CARBON TETRACHLORIDE BY THE FUJIWARA REACTION

THE Fujiwara colorimetric test for chlorinated hydrocarbons, based on their reaction with pyridine and sodium hydroxide, has a large number of modifications. These have involved the concentration and relative amount of sodium hydroxide solution used, the time and temperature of heating and the time of standing before comparison of the colour produced. The test is not specific for any one hydrocarbon, but, by modifying the procedure somewhat, conditions can be found that change the relative sensitivity towards the individual hydrocarbons.

The authors of most of the papers that have been published have elected to adopt a procedure in which the relative amounts of pyridine and aqueous sodium hydroxide are such that the final mixture remains in two phases, the colour of the pyridine layer being evaluated after separation of the two layers. By using a comparatively small volume of aqueous sodium hydroxide, the reaction mixture remains in one phase, thereby making the procedure simpler and more reproducible. Variation in the relative amount of water to pyridine results in a change of the relative sensitivity of the test towards some of the chlorinated hydrocarbons. Carbon tetrachloride is particularly dependent on the conditions used, the optimum for which we have found to be, as applied to the determination of its vapour in the atmosphere, as follows.

To 10 ml of analytical-reagent grade pyridine (free from water), containing 0.1 to 1.0 mg of carbon tetrachloride, in a 6-inch  $\times$   $\frac{3}{4}$ -inch thin-walled test-tube add from a burette exactly 0.4 ml of 0.1 *N* sodium hydroxide. Mix thoroughly and lightly stopper with a cork. (A slight turbidity will persist at this point.) Heat the tube in a boiling-water bath for 15 minutes and then add 5 ml of water and cool in running water to room temperature. Measure the optical density of the solution in an absorptiometer with use of Ilford No. 604 (green) gelatin filters, and determine the carbon tetrachloride content from a calibration curve prepared from known amounts of carbon tetrachloride in pyridine solution treated in a similar manner.

Under these conditions, the test is of about equal sensitivity for trichloroethylene, tetrachloroethane and carbon tetrachloride, although it is still about three times as sensitive for chloroform. The initial deep colours produced by trichloroethylene and tetrachloroethane gradually diminish during the 15-minute heating period. If the same amount of sodium hydroxide, but in a more dilute form, is used for this test and a shorter heating period is used for the development of the colour, the sensitivity towards chloroform, trichloroethylene and tetrachloroethane is greatly increased compared with that for carbon tetrachloride, which under these conditions is almost negligible.

These facts do not appear to be generally known and it is presumably for this reason that the author of a recently published paper<sup>1</sup> claims that carbon tetrachloride does not give the Fujiwara reaction. Jensovsky maintains that any colour produced is due to an impurity present, which he suggests may be chloroform. We have, however, shown that, under the conditions of test that we use, as described above, the presence of 25 per cent. of chloroform in the carbon tetrachloride would be required to give a colour double that produced by carbon tetrachloride alone. It is admitted that the test, even under optimum conditions, is less sensitive for carbon tetrachloride than for chloroform, but we wish to record that under these conditions it does respond to the Fujiwara reaction and that we have been unable to reduce this response by careful fractionation of the analytical-reagent grade of this material. Infra-red examination of the middle fraction showed the absence of chloroform or related materials.

Another recent paper, by Hildebrecht,<sup>2</sup> describes a method for the determination of chloroform in carbon tetrachloride by the Fujiwara reaction. The author does not claim that carbon tetrachloride will not give the reaction, but only that the conditions he has chosen are such that interference by carbon tetrachloride is eliminated.

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H. K. SOUTHERN  
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## Book Reviews

THE ENCYCLOPEDIA OF CHEMISTRY. Editor-in-Chief: GEORGE L. CLARK. Pp. xvi + 1037. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1957. Price \$19.50; 156s.

This single-volume encyclopedia—a collection of about 800 articles on chemical and allied topics—is written by some 540 contributors, many of them very well known, including representatives of Government departments, learned societies, industry, universities and institutions, and some consultants. Some of the topics have several authors, each treating a different aspect. Although the subjects are essentially chemical, there are articles about “over 20 sciences that border on chemistry,” but these are treated from a chemical viewpoint. An essential feature of this book is that clarity and lack of overlap have been the editors’ aims, although these have not always been achieved. The amount of information in it is amazingly large, and this the editors attribute to the “effort and time with no monetary compensation” given by the contributors, most articles being “near miracles of condensation.”

The comprehensive nature of the book can be seen from a few random titles: Abrasion Resistance, Bacteriology, Bile Acids, Chemical Economics, Cryogenics, Debye-Hückel Theory, Documentation, Elastomers, Furans, Genes, Histochemistry, Industrial Chemistry, Keratins, Luminescence, Magnetochemistry, Microwave Spectroscopy, Nomography, Ores and Ore Dressing, Photometric Analysis, Positrons, Quanticule Theory, Racemization, Steric Hindrance, Textile Printing, Urea Formaldehyde Resins, U.S. Food and Drug Administration and Zsigmondy, Richard (1865-1929). The last two titles are examples of important types of article: first, there are over sixty articles about research institutions and foundations and official organisations in N. America, each containing much useful information about their constitution and services; secondly, there are about seventy interesting and comprehensive biographies, but it is surprising to find that some famous chemists have not been mentioned. Nearly all the chemical elements and their compounds are treated individually, each fairly fully, although the Rare Earths and the Transuranium Elements are treated as groups; however, there is a separate article on Plutonium, in addition to a substantial entry under its group.

The editors and their helpers are to be congratulated on carrying out such an ambitious task as collecting together and dealing with all these articles. I can well imagine their difficulties, especially in view of their desire to make the book “a true and up-to-date representation of the chemistry of 1956.” Inevitably in a book of this type and size, with numerous authors, there are inconsistencies of style and minor errors, especially in the names of organic compounds; for example, the formulae on pp. 748 and 749, the names of the compounds used in weed control on p. 991 and the structural formula for caffeine on p. 797, which contains too many bonds. However, this is a minor criticism and these slight errors in no way detract from the value of the book. Unfortunately, the necessarily high price of the book will restrict its circulation, which is a pity, as most chemists should find at least some parts of it interesting, and it will be a valuable addition to any set of reference books.

N. C. FRANCIS

INSTRUMENTAL ANALYSIS. By PAUL DELAHAY. Pp. xiv + 384. New York and London: The Macmillan Company. 1957. Price \$7.90; 55s. 6d.

This book is an introduction to instrumental methods of analysis and is evidently the result of the author's experience in this field. He claims that it is intended for undergraduate and graduate students and that the subject matter can be covered in from forty to sixty lectures. The latter is an extravagant claim, but does not detract from the merit of the book; it is an excellent introduction to the subject.

The first two chapters explain the scope of the work and give some theoretical principles. Then there follows a series of short monographs on potentiometry, polarography, voltammetry, with titration methods, electrolytic methods with separations by graded potential, coulometry, conductometry and high-frequency methods. The remaining chapters deal with radiation and similar methods and include fluorimetry, turbidimetry, nephelometry, Raman spectroscopy, emission spectroscopy, absorption spectrometry, X-ray methods, mass spectrometry and nuclear-radiation methods.

The electrochemical subjects are much better treated than the others, but all the chapters are good introductions to their subjects and they are characterised by lucid and concise theoretical summaries with useful practical details. Throughout the book the author has adopted the

European sign convention for potential and he clearly explains the advantages this has for the practical electrochemist.

In a work of this kind there are inevitably omissions that strike the reader forcibly; omissions that are possibly deliberate when the author in so small a space summarises so much. For example, no mention is made of Peters as the originator of the equation dealing with redox equilibrium, and, although internal electrolysis has ample mention, no reference is given to the pioneer work of Sand and his colleagues in this field. Similarly, there is no reference to microchemical electrolytic separations by potential control.

Attractive features that will appeal to the teacher of analytical chemistry as well as to the practising analyst are the problems posed at the end of each chapter and the ample references to the original literature and specialist textbooks.

A. J. LINDSEY

**ORGANIC SYNTHESIS.** An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume 37. Editor-in-Chief: JAMES CASON. Pp. viii + 109. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price \$4.00; 32s.

The collection for this year includes norbornylene; 3:4-dinitrohex-3-ene; 5:6:7:8-tetrahydro-1-naphthol; 2-chloro-2-methylcyclohexanone, 2-methylcyclohex-2-enone and isophorone oxide; stearolic, *trans*-dodec-2-enoic and 4-ethyl-2-methyloct-2-enoic acids and ethyl  $\alpha$ -nitrobutyrate; *tert*-butyl ethyl malonate and glutaric acid; ethyl benzoylacetate and diethyl benzoylmalonate; 4-diethylaminobutan-2-one; *n*-heptamide and parabanic acid; glutarimide; trichloromethylphosphoric dichloride; benzofurazan oxide, nicotinamide-1-oxide, 2-benzoylpyridine, 2-chloro-nicotinonitrile, diaminouracil hydrochloride, 5-cyano-3-*n*-heptylcytosine, 5-amino-1:4-diphenyl- and 5-anilino-4-phenyl-1:2:3-triazole; 4-hydroxybutanesulphonic acid sultone and 3-methyl-oxindole; *pseudopelletierine*.

A continuous reactor is recommended for the preparation of benzoylacetanilide and oleoyl chloride. It is particularly advantageous with reactions that proceed relatively rapidly; the short time of exposure to heat results in fewer side reactions and a better quality product than the usual batch processes.

A warning is issued that toluene-*p*-sulphonmethyl-nitrosamide always should be recrystallised and kept in a dark bottle if it is to be stored for a long period.

B. A. ELLIS

**ORGANIC SYNTHESIS.** Volume I: OPEN-CHAIN SATURATED COMPOUNDS; Volume II: OPEN-CHAIN UNSATURATED COMPOUNDS, ALICYCLIC COMPOUNDS, AROMATIC COMPOUNDS. By VARTKES MIGRDIKIAN, Ph.D. Pp. xxx + 833; xvi + 835-1822. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1957. Price \$35.00; £14 the set.

When ordering in future, it will be necessary to distinguish very clearly between "Organic Synthesis" and "Organic Syntheses." This small variation of one vowel may involve not merely a considerable difference in the price to be paid, but also a direct antithesis in the type of book supplied. The second, as is well known, gives detailed and checked directions for the preparation of a very limited number of compounds, whereas in the first, the author has set completeness as his goal; occasionally a procedure is given, but it is usually in quite general terms.

This work can best be described as the notes of an enthusiastic research chemist, amplified and set out in narrative form. Three chapters deal with reactions (Grignard, Friedel-Crafts and diene synthesis); the remaining 27 chapters are on a chemical basis, covering methods of preparation of the various classes of compounds and then their reactions. Clearly this could lead to duplication, but the author has endeavoured to minimise this by suitable, if arbitrary, arrangement of the material while the division is covered by means of a very full index. A number of topics, e.g., carbohydrates, polypeptides, ozonides, azulenes and modifications of steroid molecules without change in ring structure, are dealt with at some length in the appropriate places.

The subject matter is necessarily compressed, but is well documented; the number of references per chapter may run up to over 700. These volumes serve as a useful starting point for the general worker's searching; obviously one specialising in organosilicon compounds would find little to assist him in just over three pages. There are numerous references in passing to heterocyclic compounds, but they are not considered systematically; the author contemplates a companion volume for this increasingly important group.

The books are marred by a considerable number of minor typing errors, over and above those already listed as errata. The statement that a compound with a *cis* configuration always

has a higher density and refractive index than its *trans* isomeride was evidently written before other consideration indicated that the configurations of the 1:3-dimethylcyclohexanes based on this rule had to be reversed.

B. A. ELLIS

**CHROMATOGRAPHY: A REVIEW OF PRINCIPLES AND APPLICATIONS.** By EDGAR LEDERER and MICHAEL LEDERER. Second Edition. Pp. xx + 711. Amsterdam: Elsevier Publishing Co.; London: Cleaver-Hume Press Ltd.; New York: D. Van Nostrand Co. Inc. 1957. Price 72s.; \$11.50.

The rapid growth in the development and applications of chromatography calls for frequent editions of any book that aims to give an up to date review of the subject. This new edition is one and a half times the length of the first, and has 4000 references compared with the former 1879. It is a veritable mine of information of the work done up to September, 1956, but even so the field continues to widen and grow so rapidly that one has to consult the literature thoroughly after that date. A brief glance at the number of journals mentioned in the list of references makes one aware how widely spread are the original papers, and how thoroughly the authors have tried to include everything.

The book follows the original pattern with five divisions to deal with Adsorption, Ion-Exchange, Partition, Applications to Organic and Inorganic Substances.

Among the new features of the first division is its extension to describe the adsorption chromatography of gases with some useful tables of data for the chromatography of gases and low molecular weight organic compounds on active carbon and silica gel. There is also a section that discusses the secondary reactions caused by the adsorbent on substances as they pass through a column. It refers mainly to oxidation of organic molecules, ammonolysis and polarisation, but it serves as a sharp reminder that such effects can occur, and the need to establish that the zones as they emerge from a column are in the state in which they were in the initial mixture before it was put on the column. A similar section in the ion-exchange part again deals with this topic and emphasises that such resins should be regarded as insoluble acids or bases.

The ion-exchange section has been rewritten to give a fuller explanation of some of the principles, and extended to give the new developments of ion-exchange papers and phosphorylated papers for separating inorganic cations. There is also a useful account of the adsorption chromatography on ion-exchange resins of organic compounds, and one on the use of modified resins for specific purposes. The scanty mention of the possibilities of molecular sieves and occlusion probably does not do justice to their potentialities.

The comparatively short section on Partition Chromatography, which outlines the main principles and techniques, is followed by the division on the application to organic substances. It is, as is well known, in this branch of chemistry that chromatography received its first impetus; consequently this section is about one-third of the whole book, and includes gas-liquid partition chromatography. The material is collected together in chapters, which are devoted to the normal classification of organic compounds: hydrocarbons, acids, alkaloids, carbohydrates, amino acids, peptides, proteins and antibiotics, to name but a few at random. Here the organic chemist and the biochemist will find the answer to many problems of separation. The authors are to be congratulated for condensing into a small space such a wealth of information.

The last division on the applications to inorganic substances finds space to mention a wide variety of separations that have been achieved, and which will suggest many applications in the fields of radiochemistry, geology and chemical industry.

From the point of view of the person who wants to try any particular application of chromatography, the book fails to advise him on which particular technique to use. It is this lack of criticism of published work that the reviewer finds most irksome, and, in fact, may tend to bring chromatography into disrepute. After all, chromatography is a means of separation, and it is the quality of the separation in its broadest aspects and the ideal conditions to bring it about that the reader wants to know. If *n* methods of separation of a group of materials are given, which of these is the best or are they all equally good? The reviewer could quote examples of work mentioned that could not be repeated in his laboratory, and yet it is given a prominent position in the book, and of reliable work just barely mentioned. It would be a good thing if the authors could be more critical in their selection of material, though the reviewer realises only too well what a gigantic task this would be.

This is a book that many chemists and others will want to buy, for it is undoubtedly the most comprehensive book on the subject.

F. H. POLLARD

## Publications Received

- ELEMENTARY PRACTICAL ORGANIC CHEMISTRY. Part III. QUANTITATIVE ORGANIC ANALYSIS.**  
By ARTHUR I. VOGEL, D.Sc., D.I.C., F.R.I.C. Pp. xiv + 645-840 + Appendix, Tables and Index i-xxxii. London, New York and Toronto: Longmans, Green & Co. Ltd. 1958. Price 21s.
- BRITISH STANDARDS INSTITUTION YEARBOOK 1958.** Pp. iv + 515. London: British Standards Institution. 1958. Price 16s.
- MISES AU POINT DE CHIMIE ANALYTIQUE PURE ET APPLIQUÉE ET D'ANALYSE BROMATOLOGIQUE.**  
Edited by J.-A. GAUTIER. Cinquième Série. Pp. iv + 161. Paris: Masson et Cie. 1957. Price 2500 fr.
- BIOCHEMICAL PREPARATIONS. Volume 5.** Editor-in-Chief: DAVID SHEMIN. Pp. x + 115. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price \$4.75; 38s.
- JOURNAL OF CHROMATOGRAPHY.** Edited by MICHAEL LEDERER. Volume 1, No. 1, January, 1958. Pp. iv + 92 + Chromatographic Data supplement iv + viii. Amsterdam, London, New York and Princeton: Elsevier Publishing Co. Subscription Dfl. 57.00; 107s. 6d.; \$15.00 per volume (six issues).
- A new journal.*
- PAKISTAN JOURNAL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.** Edited by M. M. QURASHI, B.A., M.Sc., Ph.D., A.Inst.P. Volume 1, No. 1, January, 1958. Pp. 100. Karachi: Pakistan Council of Scientific and Industrial Research. Annual Subscription Rs. 15.00; single copies Rs. 4.00.
- A new journal.*
- THE EXTRA PHARMACOPOEIA (MARTINDALE).** Published by direction of the Council of The Pharmaceutical Society of Great Britain. Twenty-fourth Edition. Volume I. Pp. xxxii + 1695. London: The Pharmaceutical Press. 1958. Price 65s.
- INTRODUCTION A L'ANALYSE ORGANIQUE QUALITATIVE.** By H. STAUDINGER and W. KERN. Translated from the German by C. COUSIN. Second Edition. Pp. xviii + 188. Paris: Dunod. 1958. Price 1850 fr.
- METHODS OF BIOCHEMICAL ANALYSIS. Volume VI.** Edited by DAVID GLICK. Pp. x + 358. New York and London: Interscience Publishers Inc. 1958. Price \$8.50; 68s.
- COLORIMETRIC DETERMINATION OF NONMETALS.** Edited by DAVID F. BOLTZ. Pp. xii + 372. New York and London: Interscience Publishers Inc. 1958. Price \$8.50; 65s.

### Papers for Publication in *The Analyst*

THE Editor welcomes Papers and Notes for insertion in *The Analyst*, whether from members of the Society or non-members. They are submitted to the Publication Committee, who decide on their suitability for insertion or otherwise.

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